VTT Technical Research Centre of Finland

CoE White Biotechnology

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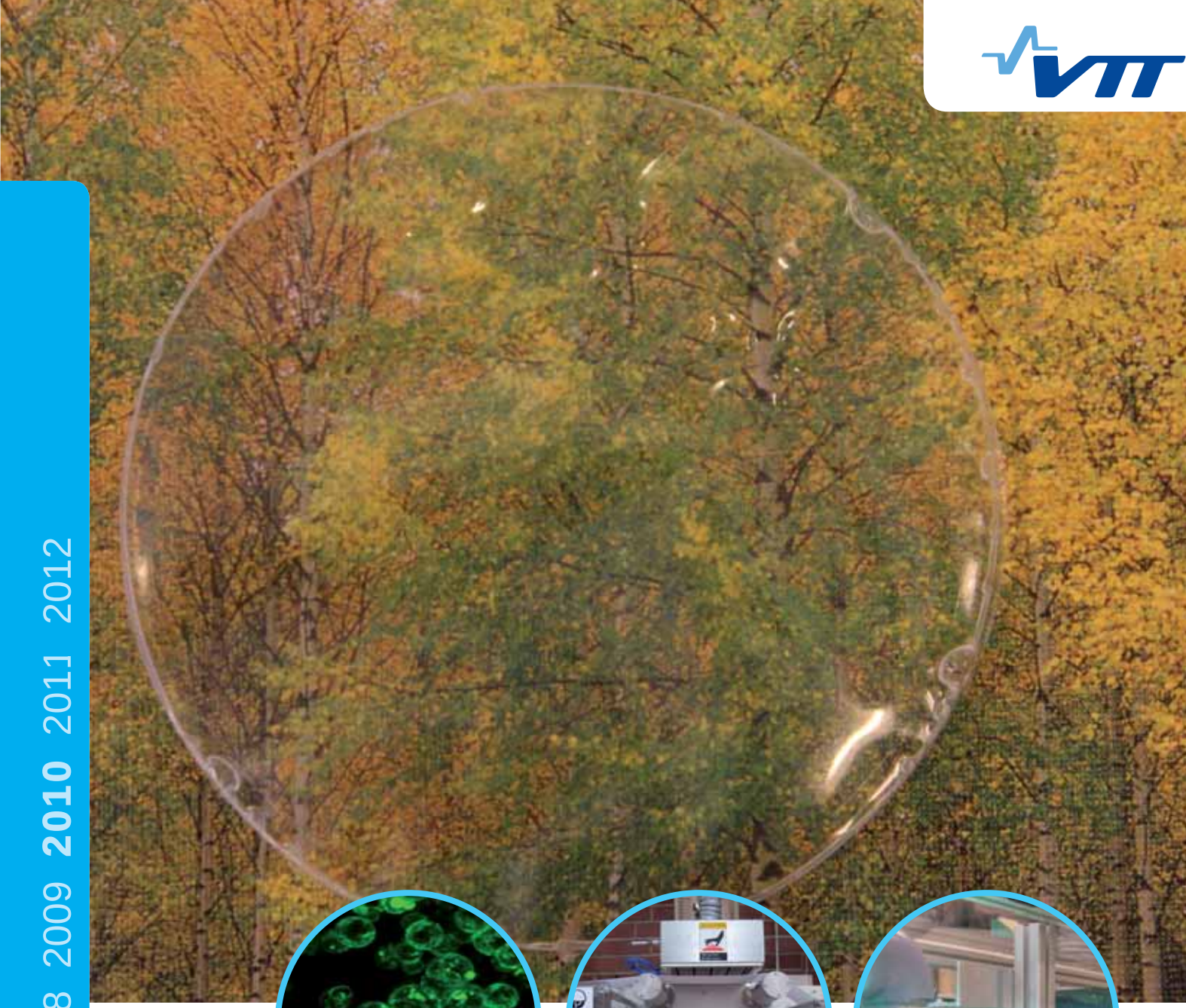
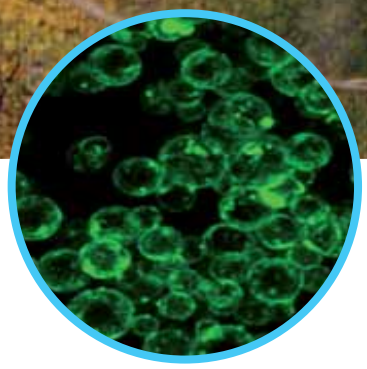
Published in:
Industrial biomaterials

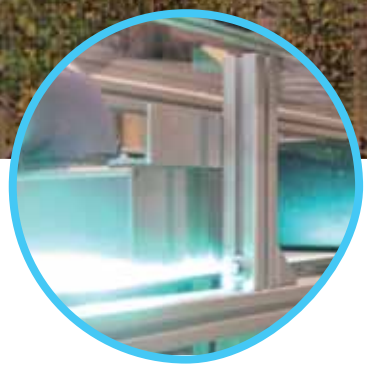
Published: 01/01/2011

Document Version
Publisher's final version

2008 2009 **2010** 2011 2012







Industrial Biomaterials

Research Highlights

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Graphic design: Tuija Soininen

Industrial Biomaterials Spearhead Programme – IndBioMat

Ali Harlin

Industrial biomaterial development enables sustainable material technology based on biomass refining and reduces oil dependence. Special emphasis is placed on the reorientation of forest industries in selected arenas. Combining emerging, modified natural polymers and biopolymers from non-food process side streams with nanomaterials, such as nanocellulose, creates a platform of hybrid materials for innovative industrial products such as packaging, appliances and construction materials. The main trends in this technology are the application of renewable resources, recycling, reducing environmental impact, and providing sustainable product differentiation and generally acceptable user-friendly products.

Industrial biomaterial research is a realisation of VTT's strategy. The focus areas in 2010 were advanced and product-oriented solutions based on renewable materials such as high-performance biopolymers, new fibre structures, and tailored functional industrial and consumer products. The Centre of Excellence of the Academy of Finland's White Biotechnology Green Chemistry formed a significant part of the research in the IndBioMat programme. SHOK activities, in particular, had an important role in the forest cluster research programmes.

Main objectives in 2010

Industrial biomaterials technology combines materials and solutions based on applying raw material efficiency with sustainable development principles. The spearhead programme combines bio-refineries and enables bio- and nanotechnology in various industrial applications of tailored biomass-based materials and converting technologies. The aims of biomaterial research at VTT are to provide technologies that enable competitive production methods to apply sustainable materials with high functionality to value-added products.

Technological, scientific and general impact goals

The main aim of the research with joint or basic funding at the VTT is to provide material technology solutions for customer approaches. The scientific level in the identified spearhead area will be raised to world-leading level, and the research activities will generate high-impact peer review publications and new, commercially interesting IPR. The overall objective of VTT's applied material technology in 2010 was to promote the competitiveness, distinguishability and sustainability of its customers.

Outcome and most important results of Industrial Biomaterials in 2010

The year 2010 was the second full year of the programme during of which the research was focused on the biocomposite future. In the field of advanced and product-oriented solutions based on renewable materials, such as high-performance biopolymers, and new fibre structures and products, the spearhead programme IndBioMat has played an important role in packaging and composite material technologies, and other novel bio-based materials for which the scientific focus has been on hybrid materials and nano-composites through bio-, chemical and nanomaterial science-enabling functionalities such as the barrier properties of bio-packaging materials. The methods for the carbon footprint calculations of the value chain were developed to assess the energy and resource efficiency, and the environmental friendliness of the alternative value chains of the forest cluster.

Technologies for the efficient breakdown of biomass into its components have been developed further. Efficient pretreatment methods were developed and their activation studied. Procedures for hemicellulose extraction from lignocellulosics were developed, as were chemical, microbial and enzymatic methods to upgrade cellulose, hemicellulose and extractives. New hydrophobic derivatives of cellulose and hemicellulose were synthesised in order to prepare barrier materials. Water vapour and

grease barrier properties of paperboard were improved with the new bio-barrier coating materials. Completely transparent and flexible films were also obtained. Lignins were modified chemically with different internal plasticisers needed in film preparation

In the area of nanocellulose, a versatile toolkit for chemical and biochemical modifications and related characterisations for nanocellulose was created. Promising results were obtained in nanocellulose applications to hybrid composite materials, films, dispersions and foams, and the related safety issues. The active publication promoted VTT's role as one of the main players in nanocellulose applications. International interest in nanocellulose standardisation has increased and VTT has started to coordinate the ISO TC229 activity in Finland. Aspects of nanotoxicology and nanosafety are addressed by a newly founded NanoTaskForce.

One the most significant achievements was the advances in functional coatings. Bio-based polymer dispersions suitable for oxygen- and water-barrier coatings of paperboard, leading to marked advancements, were developed. The use of Atomic Layer Deposition, ALD, in combination with a plasma deposition technique, was demonstrated on a small scale to improve the functional properties of packaging materials. Another remarkable achievement was the progress of bioactive paper and its production processes to a demonstration stage aimed at commercialisation. The foreseen application areas of bioactive paper demonstrators are a good example of the possibilities for other paper products.

Development of offerings in Industrial Biomaterials

Packaging business coordination has been intensified between Industrial Biomaterials and Re-invent paper programmes, the Printo Centre and intelligent printing commercialisation as well as customer solutions. The packaging industry has established a technical advisory broad, and VTT has asked to join the work as a main research institute.

Future focuses were determined in internal workshops of novel fibre material and biocomposite research. The competence in processing and modifying wood fibres for fibre-reinforced composites was further strengthened with the concurrent focusing of the direction of VTT's biocomposite research. The importance of combining nanotechnology and biomaterials was obvious. Nanocellulose activities were coordinated internally, and public nanocellulose research was promoted in the strategic research. VTT has a strong role in novel methods to fractionate and upgrade wood components, especially cellulosic fibres, hemicellulose and functional low-molecular mass components, into materials and chemicals, and this continued at full capacity. Research into biopolymer and bio-based material foams was accelerated through investment.

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CoE White Biotechnology – Green Chemistry (CoE WB-GC)

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The Finnish Centre of Excellence in White Biotechnology – Green Chemistry Research is a status that was given to VTT by the Academy of Finland for the years 2008-2013. The CoE is committed to developing new biotechnological and chemistry methods for the efficient production of chemicals and materials from renewable natural resources. 'White' or industrial biotechnology combined with 'green chemistry' has a vital role to play in developing sustainable production processes that can help save energy and the environment.

A considerable improvement is needed in the efficiency of bioprocesses before they can be considered a serious alternative to petrochemical industrial processes. One of the challenges is to make microbes, i.e., the production organisms used in bioprocesses, convert the sugars contained in biomass into the required compounds as effectively as possible. This development effort requires a wide range of skills and knowledge from biosciences to engineering. The CoE brings together the relevant expertise available at VTT in the fields of biotechnology (molecular biology, enzymology, bioprocess technology), chemistry (synthetics, polymer chemistry), systems biology (bioinformatics, mathematical modelling) and engineering sciences (micromechanics, measurement technology, nanotechnology).

The CoE's aim is to develop new technologies for the production of new biomaterials. Microbial cells are engineered to produce useful new compounds out of plant biomass sugars. Sugar acids and their derivates are produced by applying the tools of genetic technology to engineer the metabolism of microbes. These compounds have many industrial applications, for instance, as precursor molecules in the production of new bioplastics. The produced molecules are then further modified chemically and used in material applications (e.g., cross linkers in absorbent applications) or polymerised into new biopolymers. The CoE also has two important supporting activities. One is to develop sensitive measurement techniques, e.g., new measuring devices based on micro- and nanotechnologies that can be used to measure and control the productivity of microbes in bioreactors during production. Another is to use genome-wide methodology and bioinformatics to understand cell function, and mathematical modelling to generate (predictive) mathematical models of the production organisms.

The first 2.5 years of CoE activities were evaluated in June 2010 by international Scientific Advisory Board members. The evaluation was very positive and encouraged the CoE to proceed further with the planned activities. The evaluators appreciated the interactions between the different disciplines, such as biotechnology and chemistry, and considered that "the establishment of new routes for production of new valuable compounds from renewable resources has opened a highly fruitful development". The CoE also "presents an impressive list of publications, many of it in very good international peer reviewed journals, and several patent applications and notifications of inventions demonstrate a very good degree of exploitation of results". The Academy of Finland granted a three-year continuation period for the CoE for the years 2011-2013.

Some of the key CoE achievements during 2010 include:

- The improvement of sugar acid production from biomass sugars by different fungal species. Xylonic acid can be produced at > 90g/l with yeast, showing the industrial feasibility of this production system.
- The demonstration of biotechnological production of emerging monomers with yeast. These new monomers are valuable in bioplastics production, their polymerisation and resulting good polymer properties have been demonstrated.

- Chemical conversion of sugar acids into monomers for polymerisation through esterification and acetylation and the preparation of diallyl diamide derivatives. These approaches are aimed at the use of sugar acid derivatives in polyesterifications and as cross-linkers with cellulose and xylan in the preparation of novel bio-based hydrogels.
- The generation of an extensive and unique lipidomics dataset for yeast in respect to oxygen availability. Lipid composition is expected to affect stress tolerance and the passage of acids through the cell membrane.
- Granting of a VTT's Frontier program project for the MEMS breeding station development. These novel miniaturised devices are aimed at accelerated evolution and the selection of improved production strains such as robust and tolerant hosts for acid production.

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Future Biorefinery (FuBio) Program

Nikals von Weymarn

Forestcluster Ltd., one of the six Strategic Centres for Science, Technology and Innovation in Finland, was established in 2007 to coordinate the implementation of the National Research Strategy of the Finnish forest sector. Forestcluster Ltd. is owned by nine companies in the forest industry, VTT, the Finnish Forest Research Institute Metla and eight universities.

Future Biorefinery (FuBio) is one of the main research directions of Forestcluster Ltd. The main objective of the five-year FuBio entity is to establish globally-competitive knowledge platforms in Finland for the renewal of the existing forest industry and the creation of new business. FuBio focuses on biomass-based materials and chemicals to be applied in substantial global markets. The potential markets in focus include some that are well known to the forest industry (e.g., fibre-based packaging) as well as essentially new markets (e.g., textiles, nonwovens, polymers, resins and thermo-formable composites).

The actual R&D within FuBio was initiated in March 2009, when the first, two-year joint research program (FuBio 1) was started. It has a total volume of app. 19 M€. The main financers of FuBio 1 are Tekes (the BioRefine program) and the industrial owners of Forestcluster Ltd. The current program will come to an end in spring 2011 and planning for the continuation is thus well under way.

VTT has a significant role in the execution of FuBio, in R&D as well as the management of the program. VTT's input into FuBio is part of the Industrial Biomaterials spearhead programme. The specific areas of interest for the FuBio program are specified by the content of so-called Themes. FuBio comprises four Themes focusing on wet laboratory work, namely 'Fractionation technologies', 'Cellulose for material applications', 'Hemicelluloses for materials and hydroxy acids' and 'Biochemicals for protection of products and health'. FuBio also includes a Theme focusing on desktop work (management, process modelling, etc.). VTT is active in all of the Themes of FuBio.

The main achievements of FuBio so far:

- The start-up and implementation of FuBio 1 has proceeded well. Practical indications of the activity include, e.g., scientific publications, conference posters, invention notifications, three patent applications, researcher activity at FuBio seminars, Theme and WP meetings, international recognition, and cost realization.
- The cooperation between different groups has clearly intensified.
- The Finnish R&D and testing platform have been upgraded with equipment investments amounting to app. 700 k€.
- Strategic international R&D cooperation in the selected areas has commenced well and is thus making the FuBio knowledge platform stronger.
- During 2010, the Forestcluster Ltd. partners have refined and improved the general FuBio plan, which now identifies a continuation (FuBio 2) comprising five separate entities, built to resemble, more or less, future industrial value chains.

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Development of advanced biorefinery schemes to be integrated into existing industrial fuel-producing complexes

Vesa Arpiainen

BIOREF-INTEG was a 'Coordination and Support Action Project' within the framework of the FP7 program (Theme Energy). The project was funded by the European Commission from June 2008 until May 2010 and was coordinated by the Energy Research Centre of the Netherlands (ECN). It was supported by 12 partners. The main aim of the project was to develop advanced biorefinery schemes to be integrated into existing industrial fuel-producing complexes. The Final Reporting of the BIOREF-INTEG project has still not been accepted by the European Commission.

The biomass processing sectors considered in the BIOREF-INTEG project were bioethanol, biodiesel, pulp and paper, conventional oil refinery, power production, the food industry and the agrosector. For each of the sectors, one or two reference cases (existing industrial complexes) and up to three integrated biorefinery cases were defined. This has resulted in 11 reference cases and 14 integrated biorefinery cases.

The BIOREF-INTEG project included six work packages (WP). WP4 (technical, economic and ecological assessment of advanced biorefinery concepts integrated into existing industrial complexes) was the largest work-package project led by VTT. For the seven different sectors, one of the project partners was the leading party (subtask leader) in WP4.

The reference cases from the pulp and paper sector were softwood and hardwood sulphate pulp mills. The biorefinery cases (lignin extraction, dimethyl ether production via black liquor gasification and ethanol from softwood pulp) in this sector were based on the softwood pulp mill. The subtask leader in this sector was Innventia from Sweden, and the other partners were Energiteknisk Centrum i Piteå (ETC) from Sweden and VTT from Finland. The softwood reference case, and the lignin extraction and ethanol from softwood pulp biorefinery cases are reported here in the Industrial Biomaterials programme using public information from the EU BIOREF-INTEG project.

The production costs were evaluated for the reference case process and the biorefinery case processes with a modified cash flow model. No subsidies were taken into account in these evaluations. The production costs were evaluated for new pulp mills. According to these estimates, the market pulp can be produced at lower prices in the lignin-extraction and dimethyl ether (DME) production cases. The ethanol case is a better option when applied to older pulp mills for which the investment cost is low (close to zero) rather than to new pulp mills.

The integrated biorefinery cases, especially lignin extraction and black liquor gasification with dimethyl ether (DME) production, are very promising alternatives when looking at their technical state of development, economics of production and environmental impacts. The raw material for biofuels and biochemicals in these cases comes from non-food sources.

Softwood sulphate pulp mill (existing industrial complex)

Modern market pulp mills produce a considerable energy surplus and have significant potential to be energy suppliers to other industries and society. The energy surplus in the mill can be exported in different ways: biofuels (bark, lignin, electricity, etc.) and heat for district heating. The reference case is based on a chemical pulp mill producing pulp through the Kraft process. The reference mill is a hypothetical pulp mill representing existing, best-available and commercially proven Nordic technology in 2004. No fossil fuel is used in the pulp production. In older pulp mills, the fuel for the limekiln is usually natural gas, but in this reference case, the limekiln fuel is fuel gas originating from bark gasification.

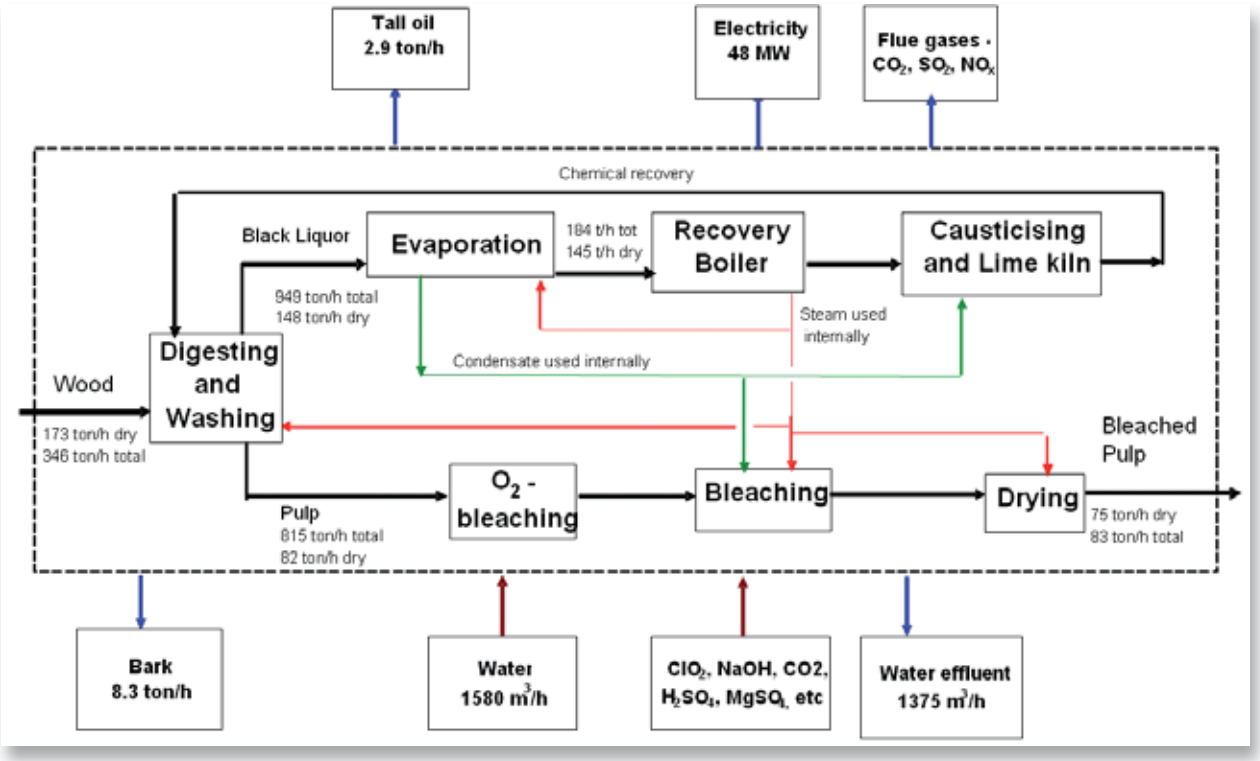

Figure 1. Block diagram reference case (softwood) for the pulp and paper sector.

The block flow diagram of the softwood-sulphate pulp mill is given in Figure 1. It should be noted that for practical reasons, not all the internal process flows are shown in this figure. Innventia used the WinGEMS software in the flowsheet simulation.

Lignin extraction from black liquor (biorefinery case)

There are three reasons for the introduction of the LignoBoost concept: to use an energy surplus in the mill for biofuel export; to reduce the load on the recovery boiler, which may enable an increase in pulp production; and to remove the mineral oil from the mill by introducing lignin as biofuel in the limekiln.

The block flow diagram of the lignin-extraction biorefinery concept is given in Figure 2. It should be noted that for practical reasons, not all internal process flows are shown in Figure 2.

Lignin is extracted from the black liquor in the evaporation plant at 30-45% dry substance. The lignin is separated by lowering the pH by injecting CO_2 (g). Lignin then precipitates and is separated from the black liquor in a filter press, re-suspended in an H_2SO_4 solution and then washed again. The remaining black liquor is recycled back to the evaporation plant. The produced lignin has a very low content of ash (<1.5%) and sulphur.

If lignin is precipitated, the heating value of the black liquor will decrease and the recovery boiler will generate less high-pressure steam. If the recovery boiler is the bottleneck of the pulp mill, which is quite common, there is a potential of an increase in pulp production of approximately 25% as the load on the recovery boiler decreases when lignin is extracted from the black liquor. The increase in pulp production is of course only possible if all the other equipment can handle the increase.

Many pulp mills use heavy fuel oil or natural gas in the limekiln, the last big consumers of fossil fuel in the pulp industry sector. The extracted lignin is an excellent fuel for use in the limekiln, and it can replace fuel oil used in other pulp mills or be sold as a solid biofuel. The limekiln fuel in the reference case and the biorefinery cases uses gasified bark, so, in this case, the lignin is sold externally.

The LignoBoost demonstration plant in Bäckhammar, Sweden, opened in January 2007. The demonstration plant can produce up to 4,000 tons of lignin per year,

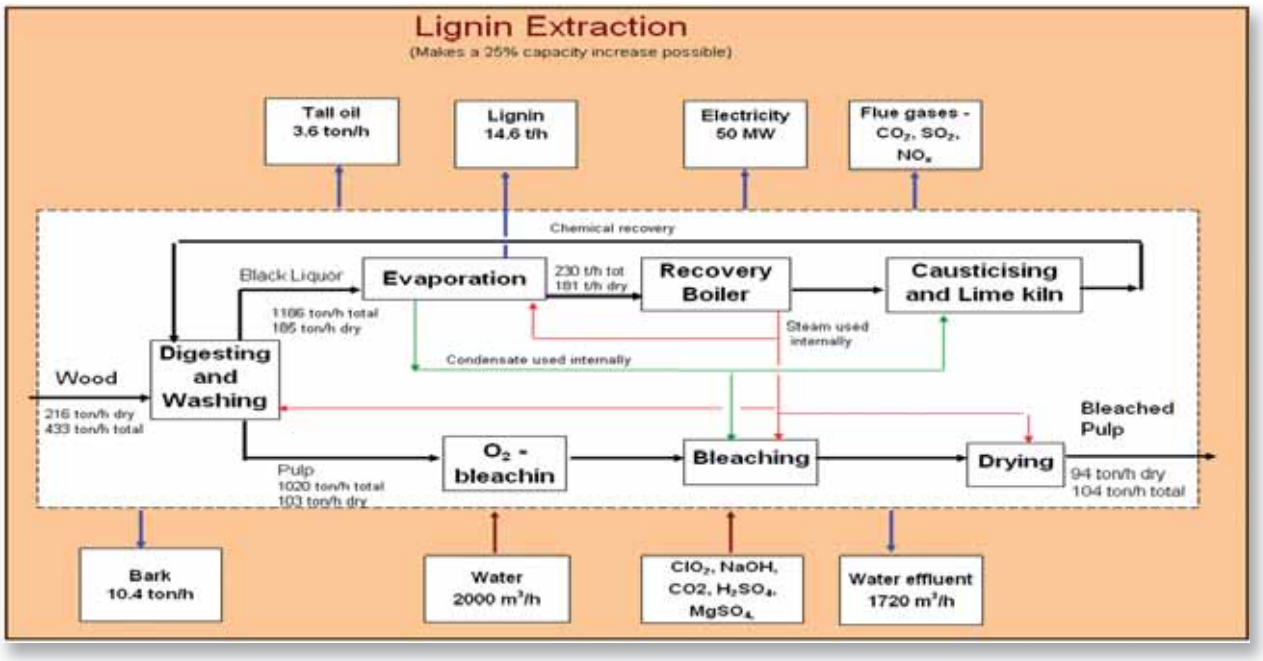

Figure 2. Process flow block diagram of the biorefinery concept, lignin extraction.

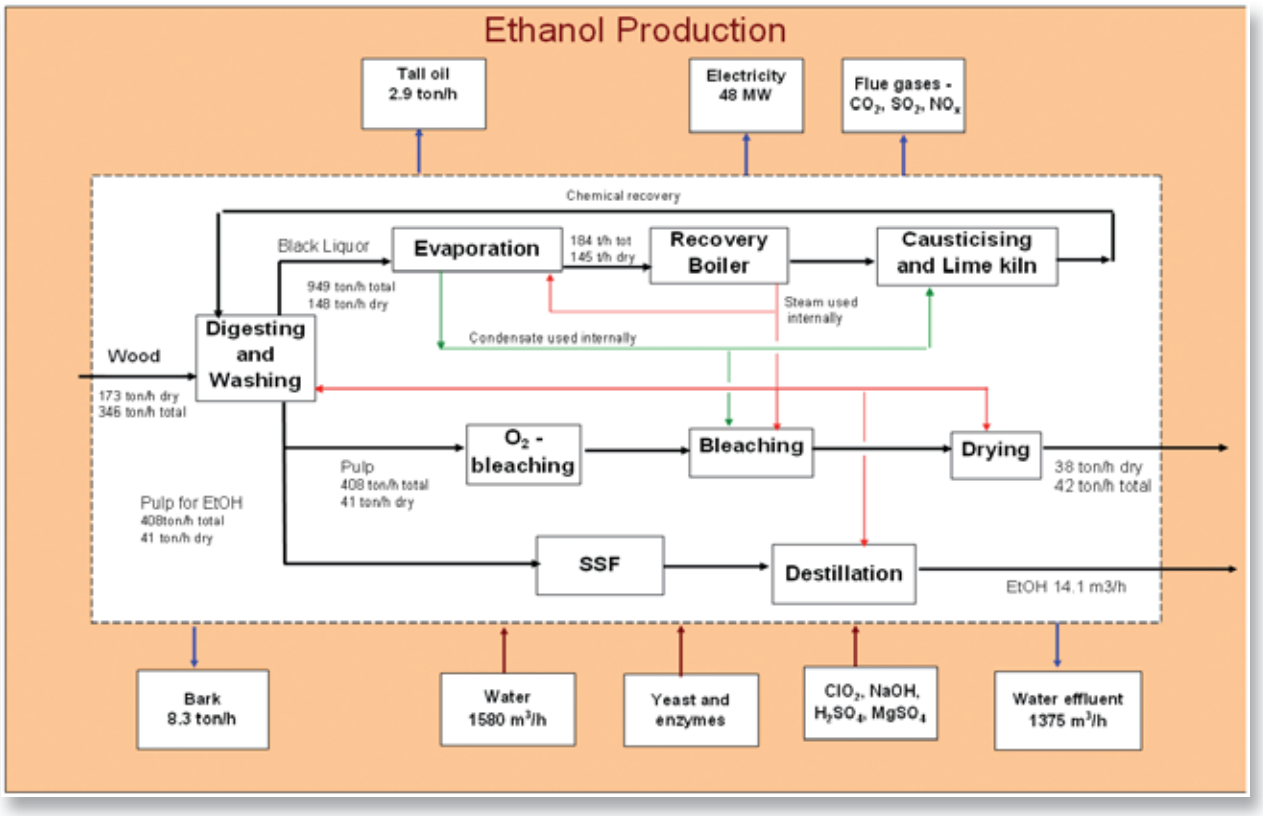

Figure 3. Process flow block diagram of the biorefinery concept, ethanol production from the pulp case.

Table 1. Production costs of softwood market pulp for the reference case and biorefinery cases.

Case	Production cost of softwood pulp, €/t
Reference case – pulp from softwood	
Production cost of market softwood pulp (10 wt-% moisture)	367
Market value estimate for market softwood pulp	500-550
Biorefinery case – lignin extraction	
Production cost of market softwood pulp (10 wt-% moisture)	319
Biorefinery case – black liquor gasification	
Production cost of market softwood pulp (10 wt-% moisture)	330
Biorefinery case – ethanol from pulp	
Production cost of market softwood pulp (10 wt-% moisture)	566

which is used for large-scale tests. For example, lignin has been used in long-term trials (2007-2008) to replace coal in a combined cycle heat and power plant in Stockholm, Sweden. Another example is full-scale trials in a limekiln in Sweden where the replacement of fossil fuel was evaluated. The LignoBoost process is owned and developed by Metso Corporation.

A full-scale plant for the LignoBoost process is planned in the Södra Cell mill in Mörrum, Sweden. The unit is planned to be in operation in 2011. The main challenges for achieving optimal economics in the process are to minimize the use and thus the cost of H_2SO_4 and CO_2.

Ethanol co-produced in a pulp mill (biorefinery case)

As the worldwide production capacity of pulp is greater than the current demand, it may be beneficial to convert a pulp mill to produce ethanol instead of pulp. Some mills have several pulp production lines, and one option is to convert one of these lines to ethanol production. The chemical recovery line is intact, but the fibre line is replaced with new units, for example, a pH-adjuster and fermentation stage. The raw ethanol produced is distilled.

The block flow diagram of ethanol from pulp case is given in Figure 3. It should be noted that for practical reasons, not all the internal process flows are shown in the figure.

In the investigated case, one fibre line is converted to an ethanol production unit. The pulp production is then halved, and ethanol is produced. When installing this concept in an old mill, much of the equipment from the pulp production can be used for ethanol production, resulting in a fairly low investment cost. In this case, when building a new plant, the investment cost will be very high. The by-products may also be used more efficiently. For example, the CO_2 produced from the fermentation may be used in a LignoBoost unit, and the effluent may be used for biogas production. This has not been taken into account in this study.

There is a pilot plant for the production of ethanol from wood in Örnsköldsvik, Sweden, operated by SEKAB, which has a capacity of 145 m^3 of ethanol per year, and a larger demonstration plant is planned. One of the main challenges is to find suitable enzymes for the saccharification step and to increase the yield by developing yeast that can use C5 sugars.

Economics and fossil CO_2 emissions avoided by producing bioproducts

The production costs of market softwood pulp were evaluated for the reference case process and the biorefinery case processes with a modified cash flow model. No subsidies are taken into account in these evaluations. The production costs were evaluated for new pulp mills. The results of these evaluations are given in Table 1. According to these estimates, the market pulp can be produced with lower prices in the lignin extraction and

Table 2. Annual avoidance of fossil CO_2 emissions from products when used as a substitute for the fossil fuels.

Case	Fossil CO_2 emission avoided, t CO_2/a
Reference case – pulp from softwood	
Bark replacing heavy fuel oil use	98,400
Electricity replacing heavy fuel oil use	301,400
Total	400,000
Biorefinery case – lignin extraction	
Bark replacing heavy fuel oil use	98,800
Lignin replacing heavy fuel oil use	185,800
Electricity replacing heavy fuel oil use	25,1200
Total	536,000
Biorefinery case – black liquor gasification	
Dimethyl ether replacing gasoline	579, 800
Total	580,000
Biorefinery case – ethanol from pulp	
Bark replacing heavy fuel oil use	98,400
Electricity replacing heavy fuel oil use	301,400
Ethanol replacing gasoline	185,500
Total	585,000

black liquor gasification case. The ethanol case is a better option when applied to older pulp mills for which the investment cost is low (close to zero) rather than to new pulp mills.

The avoided fossil CO_2 emissions for the different alternatives studied are given in Table 2. Fossil-based fuels and electricity can be replaced in all the cases. The avoided fossil CO_2 emissions are higher in the integrated biorefinery cases than in the reference case.

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Techno-economic evaluation and opportunity assessment of biorefinery concepts – Fubio cases

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Five biorefinery concepts were analysed during this study. The analysis consisted of a value chain analysis, a technical evaluation using process simulation, an economic feasibility study based on the probability calculation and a qualitative opportunity assessment. The studied cases used xylan as barrier material, galacto-gluco-mannan as a paper chemical, tannin for resins and cosmetics, and dissolved cellulose and wood in ionic liquids in order to produce clear films.

The end-product price was the dominating factor when economic feasibility was considered. The energy needed to concentrate the diluted solutions was an important factor when the technical aspects were studied. The opportunity assessment showed that the cases are sensitive to the overall concept, not just the technology or economy of the cases. This would emphasise a wider look at different aspects through the value chain when R&D-related decisions made.

Figure 1. Iterative modelling process.

Background

This study is part of the Fubio program, which is a multi-project entity aimed at creating new knowledge and solutions for processing wood biomass into new end products. Research projects vary from fractionation technologies to cellulose-based material applications and from hemicellulose applications to bio-chemicals for protecting goods and health.

The aim of this study was to support ongoing R&D development in the Fubio program and to facilitate communication between researchers and decision-making companies. This study was able to point out central R&D needs of the Fubio program. Ways of working include analysing technical and economic feasibilities as well as opportunities related to Fubio R&D work.

Methodology

The analysis conducted in this study included several different perspectives from value chain analysis to process modelling and from economic modelling to opportunity assessment. The whole analysis was iterative in order to ensure a rapid work pace to find results. An illustration of the modelling process can be found in Figure 1.

The value chain analyses were based on interviews with industrial and research partners, and on literature reviews. The process modelling used the mass and energy balances of the production processes to estimate the variable costs. The topology of the process and the initial values (such as yields, and chemical and utility consumptions) were obtained from the experts. The BALAS[1] process simulator was used as a tool for process modelling.

A literature survey was conducted to obtain the prices of the raw materials, utilities and products, and information on the process parts involved. The investment costs were also evaluated in this study. Economic modelling used the probability calculation methods for the assessment of business cases for products or technologies un-

[1] Balas is a steady-state process simulator suitable for process and concept evaluations of bio-based processes.

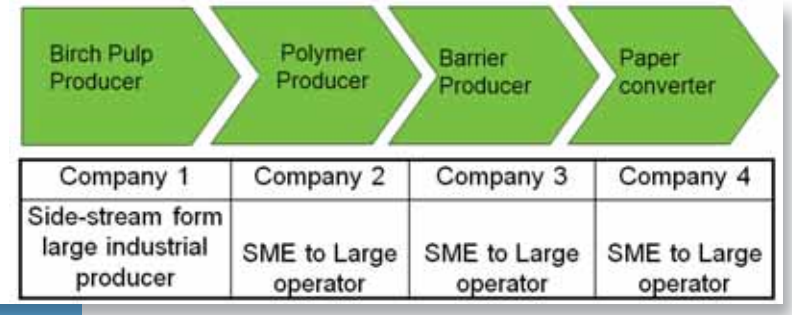

Figure 2. Value chain of Case Xylan.

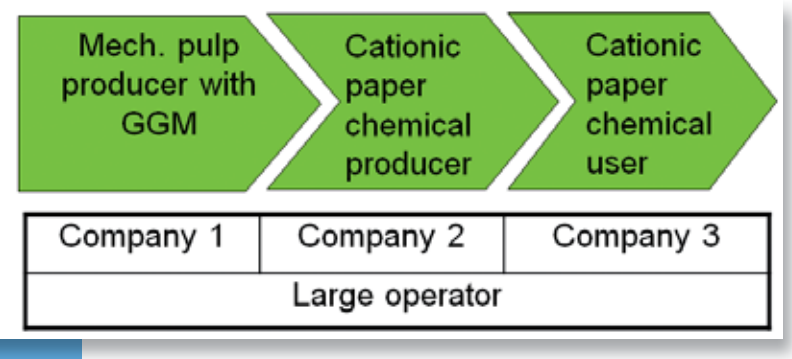

Figure 3. Value chain of Case GGM.

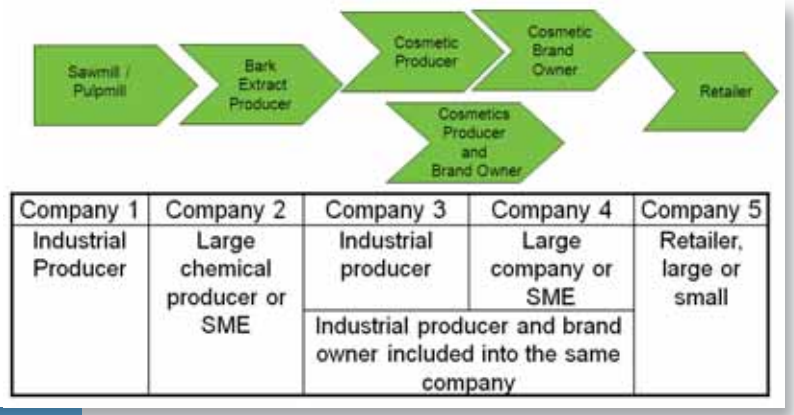

Figure 4. Value chain of Case Tannin.

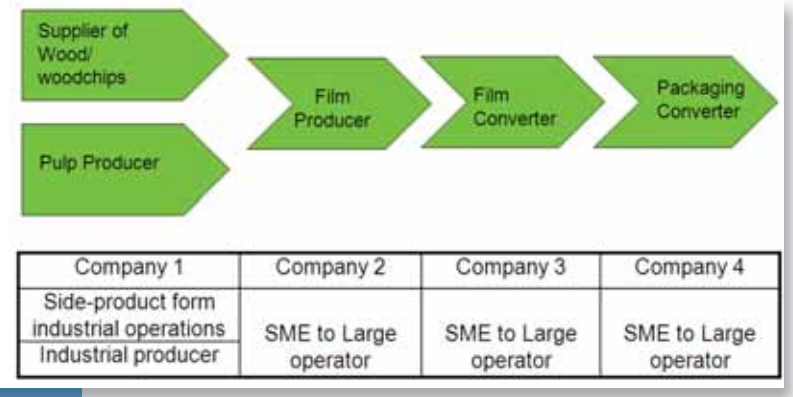

Figure 5. Value chains of Cases IL film A and IL film B

der development. In the economic model, the process and economic data were entered with ranges. A tool developed by Glocell was used for the economic evaluations.

Based on the value chain analysis, process modelling and economical evaluations, a qualitative opportunity assessment was born. The assessment was conducted based on expert opinions. A techno-economic evaluation was just a single view of the multidimensional opportunity assessment. Additional aspects such as environmental and political feasibility were also evaluated. The opportunity evaluation methodology and tool by Pöyry were used for the assessments.

The final task was to conclude the case studies and report the key findings. Several times, the first iteration of the study was not adequate, and a new iteration with redefined boundary conditions, adjusted process models, refined economic models and new opportunity assessments was needed.

Results

Evaluated cases and value chains

The cases selected for this study are described below. The case selection was performed by the industrial partners of the Fubio program. Case Xylan extracted xylan from chips and produced a barrier for paper. The modelling focussed on analysing operations undertaken by a birch pulp producer, polymer producer and barrier producer. The paper converter was considered to be the market, i.e., end-price point. The end product was grease proof paper; see Figure 2. Case GGM produced a cationic paper chemical through mechanical pulping and waste waters by fractionation and refining galacto-glocomannans (GGM). It was assumed that a paper industry company producing mechanical pulp and magazine paper would handle the entire value chain itself; see Figure 3. Case Tannin produced components for cosmetics from soft wood bark. During this study, the Case Tannin was redirected from cosmetic applications to resin applications, due to the small size of the cosmetics market. The modelling concentrated on the analysing operations undertaken by a bark extract producer as a new player in the value chain; see Figure 4. Case IL film A used ionic liquids to produce clear-film packaging from wood chips, and Case IL film B used ionic liquids to produce clear-film packaging from cellulose. The value chains of both IL cases incorporate a film producer, film converter and packaging converter. A pulp producer or supplier of wood chips keeps its business as usual. In this analysis, the packaging converter represents the end-price point.

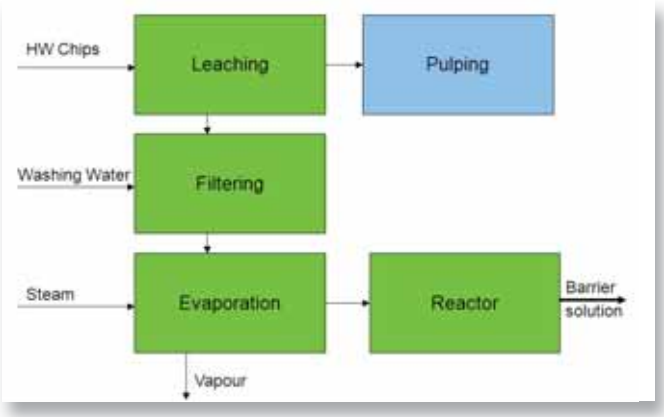

Figure 6. Production process of Case Xylan. [1]

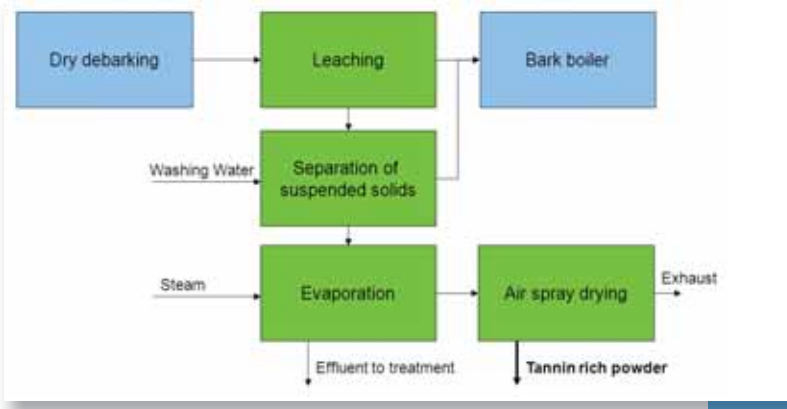

Figure 8. Production process of Case Tannin. [3]

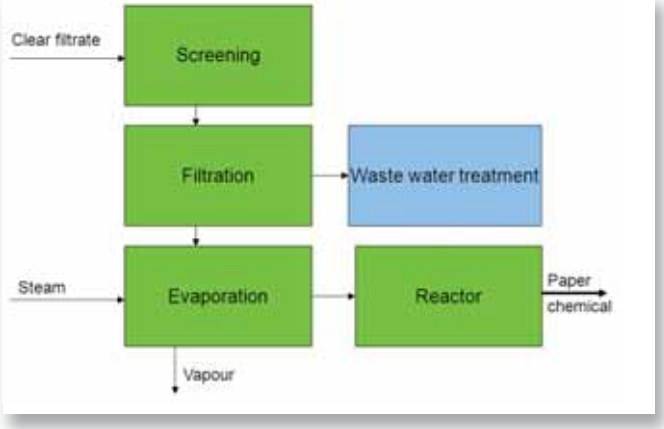

Figure 7. Production process of Case GGM. [2]

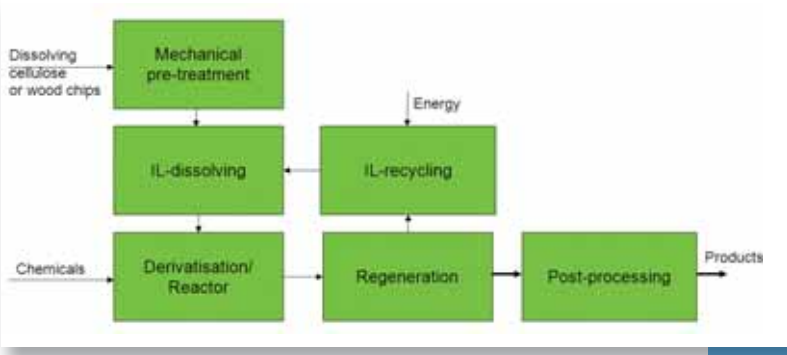

Figure 9. Production processes of Cases IL film A and IL film B. [1]

The end product is non-food packaging containing film; see Figure 5. (A reference case was also analysed during the development phase of this analysis: Case Biocelsol – enzymatic production of dissolved pulp.)

Process modelling

The production processes were sketched based on the value chain analysis. The process models were further refined together with the experts and based on the literature reviews. Case Xylan is a pretreatment for hardwood chips before pulping to remove xylan. Leached xylan is filtered and concentrated before the reactor. The end product is a grease proof barrier replacing poly-ethylene (PE). Wood chips are used for pulp production after leaching; see Figure 6. Case GGM uses the clear filtrate from the paper machine. Coarse particles are screened and GGM is separated during filtration. GGM is concentrated and then refined in a reactor. The end product is a cationic paper chemical that replaces cationic starch. GGM lean waste water is treated at the waste-water treatment plant; see Figure 7. Case Tannin makes use of the bark. Tannin is leached from the bark. Solids are separated and some of the water is evaporated from the solution. Further drying is conducted in the spray-drying unit. Tannin-rich powder is the end product, replacing phenols in the resins, or it can be used as an additive in cosmetics. Further processing may still be needed. Solid bark waste is burned in a bark boiler; see Figure 8. Cases IL Films are based on the ionic liquids, which are used to dissolve cellulose or wood chips. Derivatisation can be performed for dissolved cellulose in order to gain additional properties. After that, the cellulose is regenerated and the ionic liquid is recycled. The end product is clear film, which replaces PET-based films; see Figure 9.

Three different scenarios were calculated for each case. The normal scenario represents the assumed process conditions. The worst-case scenario is based on the pessimistic assumptions of the process conditions (e.g., low yield and high energy demand). The best-case scenario is based on optimistic assumptions (e.g., high yield and good fractionation). Based on the results of the worst and best case scenarios, the minimum and maximum values were obtained for the range of economic modelling.

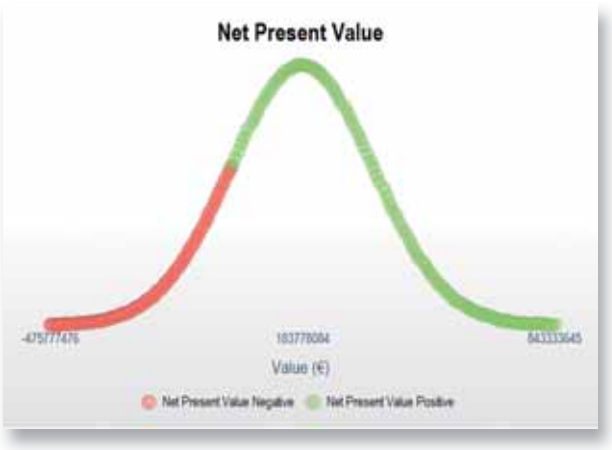

Figure 10. NPV of Case Xylan.

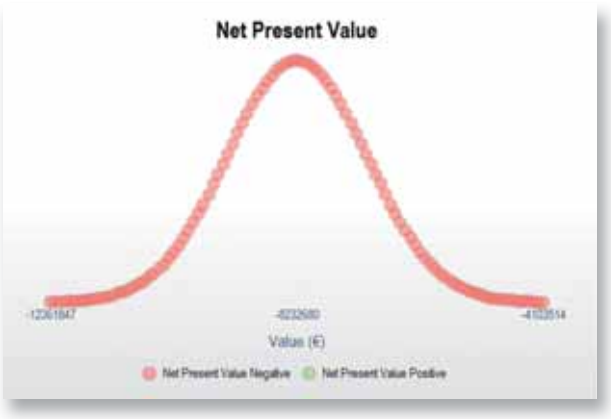

Figure 11. NPV of Case GGM.

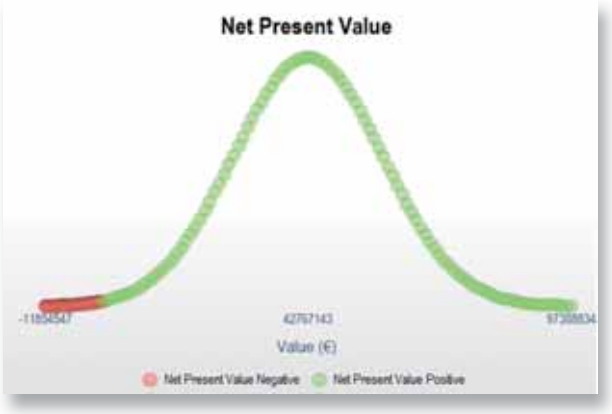

Figure 12. NPV of Case Tannin.

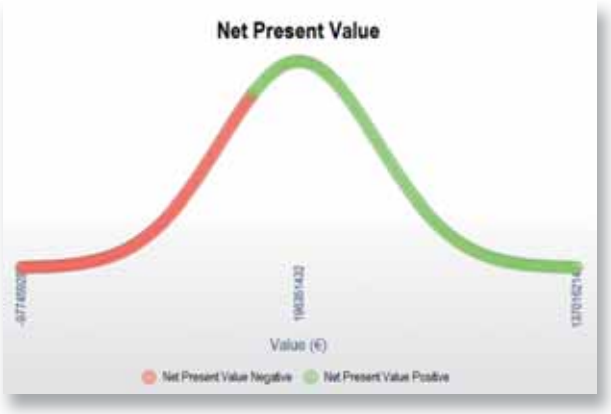

Figure 13. NPV of Case IL film B.

Economic modelling

The variable costs were estimated based on the process modelling. The raw material, end product and utility prices were collected from the literature and refined based on expert opinions. The cationic paper chemical is the cheapest end product, and film is the most expensive. Besides the more common raw materials such as NaOH and H_2SO_4, there are several case-specific chemicals, marked here as Additives. The price estimates are from Europe. The fixed costs, i.e., investment costs, of the new process concepts were also estimated. The investment for Case Xylan was 40 to 60 euros. Case GGM required an investment of 3 to 9 million euros. The investment for Case Tannin with a redefined and simplified process was 3 to 4 million euros. Cases IL film did not include estimates for investment costs. The concepts for the IL cases are still in the research phase.

The net present value (NPV) was used as an economic indicator of the feasibility of the studied concepts. A ten-year time-span was assumed. All the input parameters were normally distributed with given minimum and maximum values. As a result, a normally distributed NPV was obtained. The average NPV of Case Xylan was 186 million euros with an 84% probability of a profitable investment if the premium quality is reached. Case GGM had an average NPV of 8 million euros and no change for a profitable investment. For Case Tannin, the average NPV was 43 million euros with a probability of almost 100% of a profitable investment. For Case IL film A, the average NPV was 397 million euros, and the chance of success was 93%. In Case IL film B, the average NPV was 196 million euros and the chance of success 72%.

A sensitivity analysis was conducted during the economic modelling. It showed that the end product price was the most dominating factor of the economic feasibility of for all evaluated cases. The market size was limiting factor for tannin applications in cosmetics. Alkali consumption and recycling were the dominating cost factors for

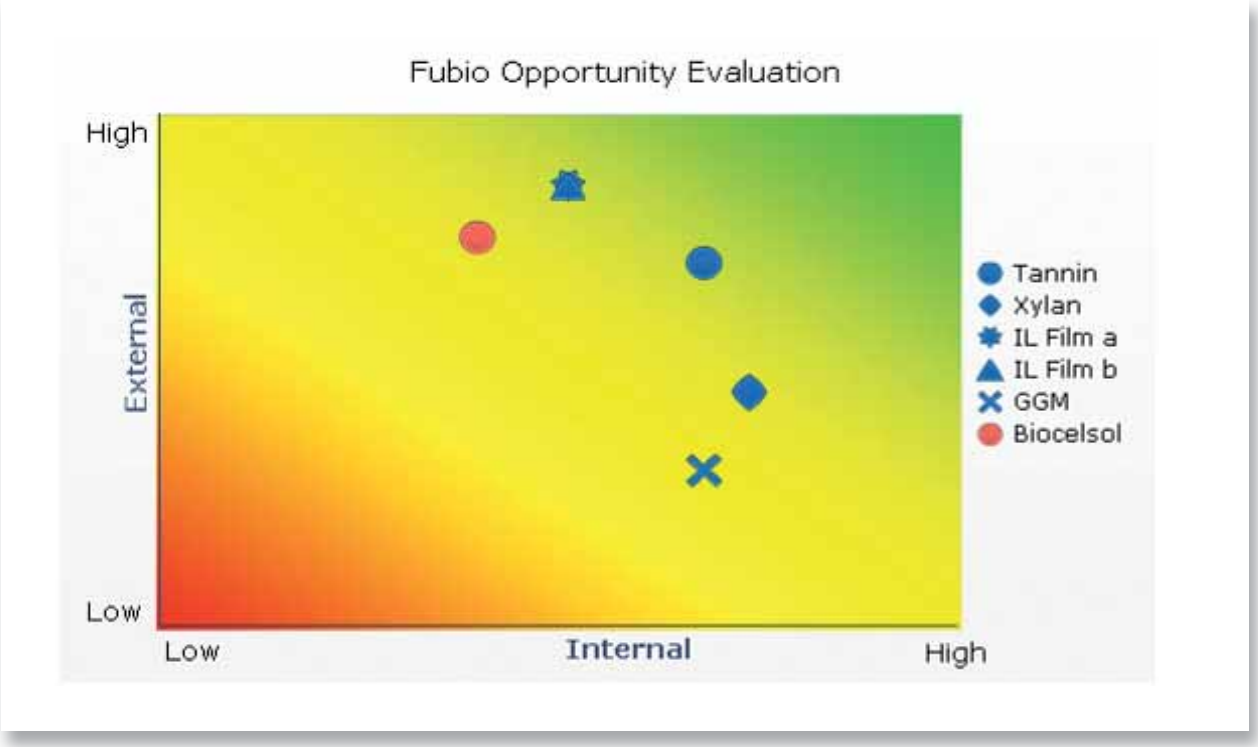

Figure 14. Opportunity evaluations of the cases.

Case Xylan. Raw-material prices and energy consumption were the dominating costs for Case GGM. When tannin was used for the resin applications, Case Tannin, the energy consumption of the production process was a dominating cost factor. When Cases IL films were conspired, the ionic liquid recycling rate and the price of the ionic liquid were major cost factors. In addition, the energy consumption of the ionic liquid recovery (such as heat used for distillation) contributed a large part of the costs.

Opportunity assessment

The opportunity assessment diversified the outlook of the studied concepts even further. Technical and economic evaluations were just two aspects of the opportunity assessment. They were called (i) technical feasibility and (ii) economic feasibility. Other aspects studied were (iii) substitution of current products, (iv) market entry, (v) expected market growth, (vi) political feasibility and attractiveness, (vii) innovativeness of the new concept, (viii) technical availability, (ix) product quality feasibility, (x) environmental and health feasibility and (xi) forest product value chain match. The aspects were divided into two groups: internal risks, which are caused by the technology or company itself (e.g., technical feasibility), and external risks, which are not company- or technology- specific (e.g., political aspects). The opportunity assessment was a qualitative study conducted by the experts. Three grades were used to score the cases: grade 0 was used for a minor opportunity, great uncertainty or big risk; grade 1 was used for a medium opportunity or risk; and grade 2 was used for a great opportunity, minor uncertainty or minor risk. The cases are comparable.

The end products of all the studied cases substituted current products. None of them was a completely new product. The easiest market entry was for Case GGM and Cases IL film. The market growth was biggest for films, Cases IL Films, and for resins, Case Tannin. The current market size is biggest for barriers, films and resins, Cases Xylan, IL Films and Tannin. Cases IL films were seen to be the most politically feasible cases. Case Tannin was seen to be most technically feasible. The best product quality was for Case Xylan. Case Tannin and Case GGM were the best fits for the forest industry value chain. All the cases were considered innovative and environmentally feasible. A notable finding was that all the necessary processing units are already available. Naturally, the process conditions need to be studied and defined. The opportunity assessment is summarized in Figures 14 and 15.

Issue	Tannin	Xylan	GGM	IL Film a	IL Film b	Biocelso
Substitution	1	1	0	1	1	0
Market entry	1	1	2	2	2	2
Market growth	2	1	0	2	2	1
Market size	2	2	0	2	2	2
Economic feasibility	2	0	0	2	2	2
Political feasibility	1	1	1	2	2	2
Innovativeness	2	2	2	2	2	2
Technical feasibility	2	1	1	0	0	0
Product quality feasibility	0	2	1	1	1	0
Environmental and health feasibili	2	2	2	2	2	2
Forest industry value chain match	2	1	2	1	1	1
Technical availability	2	2	2	2	2	2

Figure 15. Risk assessments of the evaluated cases.

Based on the opportunity assessment, Case Tannin showed the biggest opportunity of the analysed cases, followed by Case Xylan and Cases IL films as the next most promising cases. Case GGM is a challenging business case with the lowest opportunity. When Case Tannin was considered, a large growing market of resins and an economic production process were seen as opportunities. The unknown factor was the product quality of crude tannin-rich powder. Could it be used for resins or cosmetics? If additional processing is needed for the tannin-rich powder, it will affect the results of this study. The challenges of Cases IL films were internal: the technology using ionic liquids is not ready. Great external opportunities were seen for the IL cases. When the barrier materials in Case Xylan were considered, the challenges were more external concerning how to enter the current markets and how the market would grow in the future. Case GGM suffered strong competition for the starch-based cationic paper chemical. A more valuable end product would make the recovery of the GGM a more attractive option.

Conclusions

Key findings of this study were that all the cases were based on innovative products developed for existing markets. Due to this, the focus on developing end products with quality properties corresponding to market needs could be emphasized more in future R&D. The study showed that the sensitivity of the economic feasibility is dominated by the end-product price. Thus, end products of a higher quality and price have to be developed in order to make a successful business case.

When the production costs were considered, significant energy consumption was a barrier to business success in many cases. This was due to the fact that the production used very low consistency suspensions, which had to be concentrated before further processing. The concentration could be achieved using membranes, but in such cases, the high investment costs would be critical to the success. To overcome this issue, cases should be integrated into a pulp mill in which excess energy and waste water treatment are available. Successful handling of raw material logistics, infrastructure, etc. is also easier within an existing pulp/paper mill and hence supports the new business cases better than in stand-alone operations. This could also increase the profitability of the existing mill.

The developed methodology for analysing the technical and economic feasibility together with the opportunity assessments showed that that the cases are sensitive to the overall concept, not only the technology or economy of the cases. This offered researchers and decision-makers a wider look at the developed technologies and facilitated the discussion between the stakeholders. The results of this study were used when the future R&D activities were defined in the Fubio program.

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From biorefinery concepts to business opportunities

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The current research trend in bio-based fuels and chemicals is towards the emergence of a growing number of different biorefinery concepts. The methodology Sustainability of the new process options and value chains was developed to rise to this challenge. The goodness and feasibility of different concepts are analysed from various points of view including technical feasibility, business opportunities and environmental aspects. The developed methodology was applied to a special case study. Two biorefinery concepts that produced a particular product were analysed. The concepts were mainly based on the existing process equipment and the whole value chain from raw materials to end products, and they involved six different companies. The differences between the concepts were analysed and compared with the current situation. This paper outlines the methodology without going into detail on the case study.

Materials and methods

The methodology Sustainability of the new process options and value chains was developed to understand the (cross-) industry value chain from different points of view). The production process alternatives were first analysed for technical feasibility, providing a basis for various economic and environmental analyses. Business opportunities were analysed for each actor within the value chain.

Technical pre-feasibility

The overall material and energy balances are calculated based on VTT expertise, and information available in the

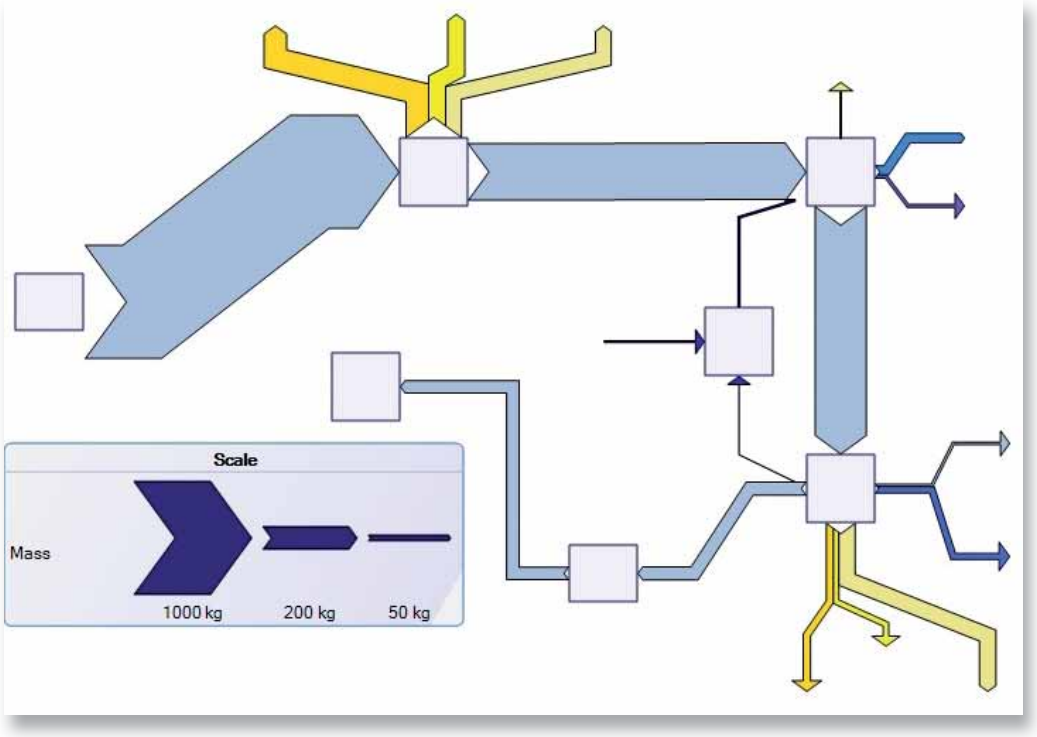

Figure 1. Example of a Sankey diagram of the mass flows in the system.

literature and from industrial partners. The work starts by specifying the level of detail of the modelling. This includes specifying the importance of different process parts, which chemical components or pseudo-components should be used in the modelling, etc. Sub-processes can be treated in a black-box manner or by using more detailed models when needed. The level of detail depends mainly on the question to be answered, the complexity of the system and the chemical components involved. The schedule also limits the simulation level to an achievable state in the given time frame. The important issues are the end products from the sub-process in question, yields for different end products, and raw materials and energy usage. The integration level depends of the case in question. A Sankey diagram is a visual tool to illustrate, e.g., mass flows and yields (Figure 1). Tools to be used include simulation software (e.g., Balas) and the Excel spreadsheet programme, to mention a few.

Sustainability evaluation

The environmental impacts of the concept, especially on climate change, are studied using Life Cycle Assessment (LCA) (EN ISO 14040:2006). It is a method for quantifying the environmental interventions of a product or production system throughout its life cycle from raw material to waste. Two different approaches can be used in the analysis: 1) consequential or prospective, and 2) attributional or retrospective[1,2]. The final environmental impact analysis can be a combination of both approaches.

The consequential approach aims to assess the change between two stable conditions. The approach ideally includes activities inside and outside the life cycle of the studied product that are affected by the change[1]. The results, the environmental impacts, illustrate the consequences of the studied actions. Key issues include the impacts of raw material competition and of putting new products on the market.

The attributional approach aims to describe the environmentally relevant physical flows that are attributed to various actions using an allocation procedure. The results of the analysis are the environmental impacts of the desired product, which can be compared with the results of other products that implement the same selected functional unit. Critical issues of the approach are the assessment from cradle to grave and the allocation of environmental burdens between products. These can be carried out in different ways. The fundamental problem of the approach is its inability to describe the impacts of any change.

Value chain and business opportunities

The analysis of the value chain and the business opportunities aims to identify the network of actors or companies needed to commercialize the products and gain an understanding of the main drivers and arguments for each actor becoming involved in developing and commercializing the technology. For example, the analysis can support negotiations with potential customers and stakeholders

The first step of the analysis is to identify the value network actors involved in the production and use of the products. The business models, product market information, raw materials and required R&D investment in technology are identified. The analysis can be carried out at a more detailed level or be based on a rough description of the phases of the production process. The basic analysis provides a preliminary understanding of the roles and business drivers of the value chain actors and potential companies. The costs and benefits of the new technology can be compared with the corresponding features of the existing business activities in the identified potential companies.

The next task is to structure potential markets, i.e., market analysis, and to identify and analyse customer values in the market area with the most potential for the technology in question. In order to gain an understanding of the potential users of the products, information about the high-level market structure. This helps to identify the most important potential customer market segments to which the new products could be offered. Customer value modelling is a qualitative analysis of business potential and value for a single actor in the value chain. The goal of customer value modelling is to identify the critical factors affecting the decision-making of the critical actors (the part of the network taking the ‘final’ decision to ‘invest’ in the new technology). The customer value of the new technology to the critical actor is the basis of the market and value analysis for other actors in the network.

The roles, earnings and business prospects of the companies in the proposed value chain are outlined and the relative importance of the companies analysed. The objective is to identify the high-level business opportunities and obstacles for the different actors and form an earnings model for these actors. There has to be sufficient motivation and payoff for each network party so that adequate collaboration can be established and maintained. The benefits for each actor and its motivation to act as part of the value chain are analysed using concepts from

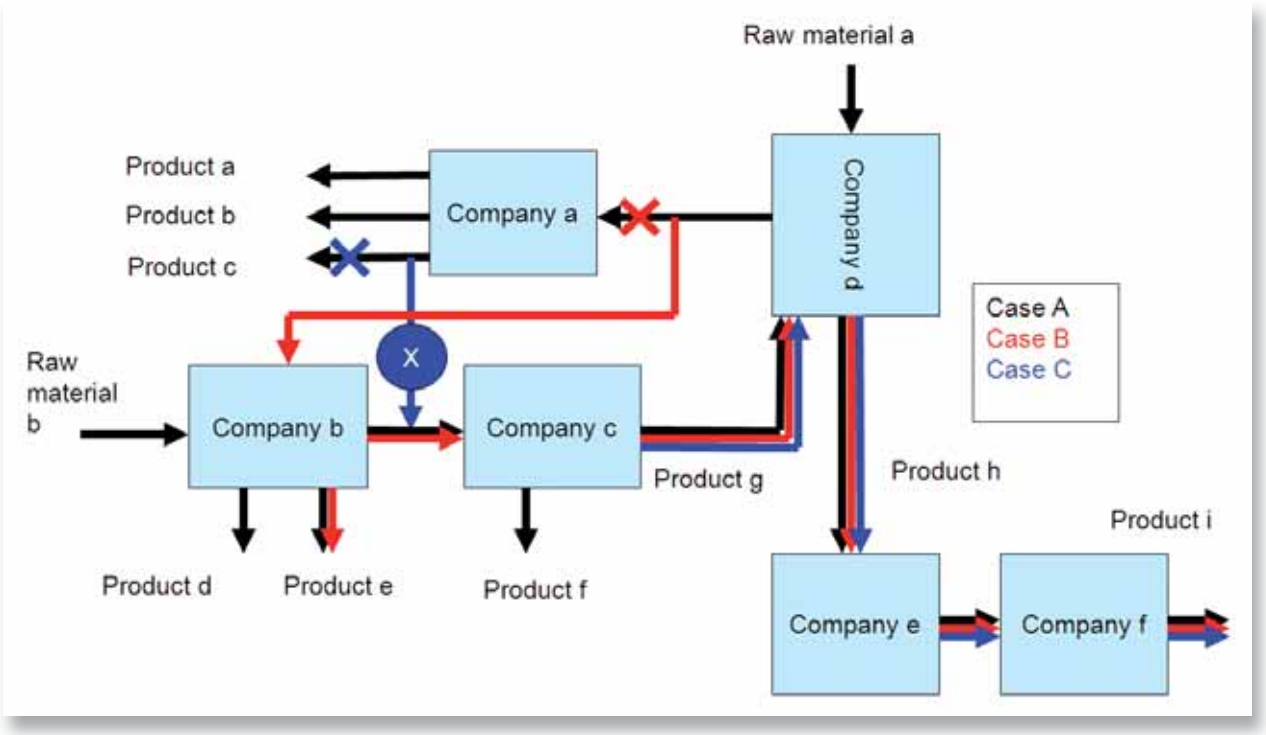

Figure 2. Illustration of the current situation and the two studied cases. The black arrows represent the current situation (case A), the red lines case B and the blue lines case C.

co-operative game theory, allowing the negotiation power and marginal benefits of different network partners to be analysed.

An interactive systems dynamics based decision support tool can be built for structural analysis, prediction, optimization, re-engineering and sensitivity analysis. For instance, different raw materials, and future scenarios and production constructions, and their effect on price and product attraction in various customer segments – and ultimately on market shares and profit – can be simulated and tested. A sensitivity analysis is used to identify the most significant factors for the system dynamics and for developing robust policies. Prediction is useful when one organization's actions cannot affect the outcome but the organization can benefit from reacting quickly to changing circumstances (such as predicting the raw material market price and reacting to it). The strength of system dynamics is that the model can consist of soft factors such as company brand, image in the market or consumer preferences for the features of products. It is possible to simulate the high-level dynamics of the value chain instead of the detailed company- or product-specific processes. System dynamic modelling has been applied to value network analysis, market dynamics simulations and innovation diffusion process simulations[3,4,5,6,7].

Results and discussion

The methodology outlined in the previous chapter was used in a case study in which a cluster of intermediate and end products was produced from a side stream of an existing process. Two different production technologies were analysed. The value chains involved several companies that are illustrated in Figure 2.

Product yields and emissions were calculated for both concepts, giving a basis for further analyses. The cradle-to-gate analysis showed that less GHG is produced in both concepts than in competing technologies (attributional approach), though they produce more GHG than in the current situation (consequential approach). The potential markets for the product are huge. The most important value chain actors were identified and they differed between the concepts.

Conclusions

The methodology Sustainability of the new process options and value chains has been developed and applied successfully to a case study. The methodology combines several different analyses and provides information on:

- mass and energy balances and yields (technical prefeasibility)

- environmental impacts, such as GHG emissions (sustainability evaluation)
- potential markets, segments and their volumes (market analysis)
- customer values, product attraction (customer value modelling)
- business prospects of the actors, fair sharing of generated values (earning model of different stakeholders)
- future scenarios, effect on price, product attraction, effects on the market, shares and profit (system dynamic modelling)

By combining the information from different tasks, an interactive decision support tool can be designed to perform structural analysis, prediction, optimization, re-engineering and sensitivity analysis of biorefinery concepts. The target actor could be a company with a vision of new concepts, e.g., resulting from basic biorefinery research. Full analyses at a detailed level through all tasks require some resources, but the methodology can be tailored to meet specific needs.

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Oxidation of lignin to biofenolates

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Different types of technical lignins are formed as by-products of processes that exploit biomaterials for various purposes, such as papermaking and bioethanol production. There is great interest in replacing synthetic materials with bio-based materials in gluing applications. Technical lignins are a cheap, renewable starting material for adhesives and glues. The thiol-ene 'click' reaction, which can produce products with unique physical and mechanical properties, was tested.

Materials and methods

For the gluing tests, softwood kraft lignin, in original and oxidised forms, was used. Lignin was oxidized at the Parr reactor with continuous stirring. Lignin with a 25% dry content was dissolved in 1M NaOH solution at 70°C using constant 5 bar oxygen pressure for ~7 minutes. In addition, the reference treatment was performed under the same reaction conditions, except the pressurized oxygen. The reference glue materials were PVAc latex (type EriKeeper) and CMC glue (wallpaper glue). The coating/lamination was tested using KCL's nozzle applicator. For the glue seam application, a slot plate was used. The substrate for the laminations and gluing was brown packaging paper. To measure the gluing strength, the peel test method (T-geometry) was used. The contact angle and drop volume were measured to see the effect on the surface properties. The water resistance was tested in alkaline (0.1M NaOH) solution using the Nessler tubes method with a Hellige Neo-Comparator instrument. The thiol-ene 'click' reaction was also tested between the ene and thiol groups under UV irradiation (λ = 254 nm). The photoinitiator used was 2,2-dimethoxy-2-phenylacetophenone (DMPA). The reaction was followed by 1H NMR.

Results and discussion

The work in the project can be divided in three main areas: a) to produce phenoxy radicals in alkali oxidations, b) to test gluing properties of oxidised lignin and c) to produce a literature survey and test reactions of thiol-ene 'click' reactions.

The hypothesis of this research was that lignin forms stable radicals. These radicals are generally recognized as the primary oxidation products of lignin. Alkaline solution at an elevated temperature was used to oxidize softwood kraft lignin. The lignin was only oxidised to the extent that phenoxy radicals were formed. To minimise secondary reactions, the treatment time was limited to ~7 minutes. The applicability of these oxidised lignins to waterproof glue/lamination materials was tested right after the oxidising treatment, and the conducting time for both the original and oxidised material was two hours. Improved gluing strength in lamination was observed when the drying temperature was increased (150°C instead of room temperature). The oxidised materials did not show any improvement in the gluing strength in the lamination. The gluing strength with oxidised lignin was even weaker than in the original lignin in side gluing. The reason for this is unclear. In side gluing, the temperature has no influence on the gluing strength. Neither the original nor the oxidised lignin created internal or cohesion strength. The effect on the surface properties was also poor for both the original and the oxidized lignin, showing in the contact angle at the time point 0.1 seconds at 24° and 27°, respectively, whereas the reference plain packaging paper showed a stable contact angle of 111°. In both the lignin samples, the water drop was absorbed by the paper, making contact angle measurements impossible at the time point 0.5 seconds. Even though both reference glues showed downward properties at the contact angle measurements, they were on a higher plane than the tested lignins. The absorption rates were also stable after 0.5 seconds for the reference glues. By the water resistance in the side gluing for the oxidised lignin with drying, a less coloured solution was observed. This was most probably caused by cross linking.

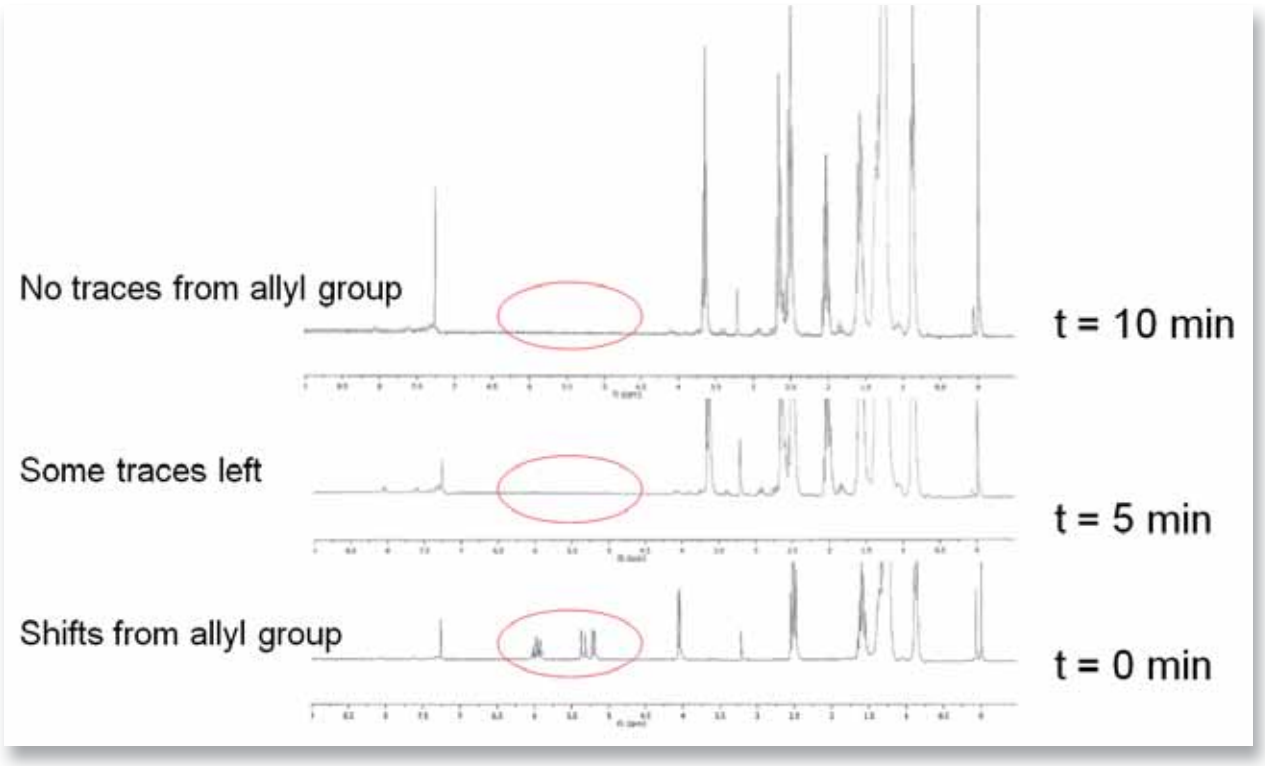

Figure 1. ^{1}H NMR spectra of the crude reaction mixtures after photolysis of allyl chloride, 1-dodecanethiol and photoinitiator.

Thiol-ene polymerizations have been studied extensively in the last century, and these reactions are known to proceed via a free radical, step-growth mechanism. Multifunctional thiols will copolymerize with almost any multifunctional ene, and the reaction mechanism affords delayed gelation, low shrinkage, high conversion, and uniform crosslink densities. This results in an ability to produce products with unique physical and mechanical properties. The literature research into thiol-ene 'click' polymerization consists of a selection of relevant articles, patents and other literature sources concerning recent thiol-ene 'click' polymerization applications and commercial applications. The test syntheses of thiol-ene 'click' reactions were performed at room temperature under a UV lamp using a 2% DMPA catalyst. Reactions were followed with ^{1}H NMR every 5 minutes. The reaction completed in 10 minutes, with the disappearance of double bonds at 5.1-6.0 ppm in ^{1}H NMR spectra (Figure 1). The reaction was very fast and even in 5 minutes, only traces of double bonds were obtained.

Conclusions

Phenoxy radicals were produced successfully in alkali oxidations at an elevated temperature. The gluing and lamination properties were tested from these oxidised lignins. Unfortunately, the gluing properties were not as good as those of the reference glues. Thiol-ene 'click' reactions were also tested, and a literature survey was produced. The thiol-ene 'click' reaction formed a stable bond between the thiol group and the double bond in 15 minutes at room temperature.

Publications

Literature research related to 'Thiol-ene click polymerization'

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Extensive view on cellulose – Cellulose-lignophenol films

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Lignophenol is a polymeric lignin derivative isolated from wood meal. Due to its size and structure, it is expected to model natural lignin better than the previously exploited small lignin model molecules. The aim of this work was to establish a method to prepare uniform cellulose-lignophenol films and tentatively confirm attractive interactions between regenerated cellulose and soluble lignophenol macromolecules. By reassembling the cellulose and lignin from solution, it is possible to study the obtained structures with respect to interaction between the polymers. The reassembly could provide, e.g., attractive mechanical properties as well as stable and ductile films. Further chemical modifications through, e.g., enzymatic actions on lignin may enable an easier route for tailored material properties when considering, e.g., barriers and membranes.

Materials and methods

The viscose solution was kindly delivered by Kuitu Finland Oy, Finland. The cellulose content of the solution was 9.1 wt-% and the NaOH content 5.6 wt-%.

Lignophenol prepared from purified softwood (*Japanese cedar*) using a two-step cresol/acetone process, as described in Funaoka[1], was kindly donated by Dr. Aoyagi, Mie University, Japan. The chemical structure and IR spectrum of the pure softwood-derived lignophenol derivative is shown in Figure 1.

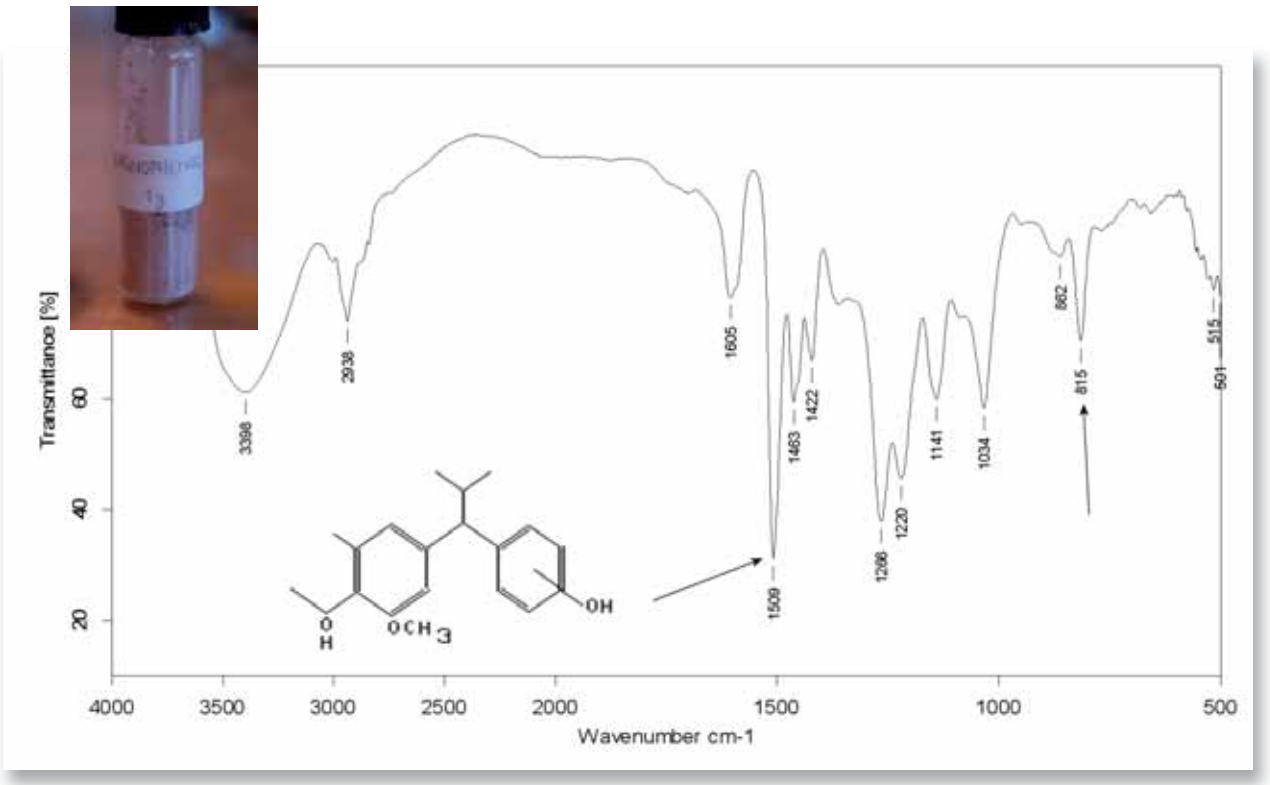

Figure 1. Chemical structure and IR spectrum of the softwood-derived, purified polymeric lignophenol.

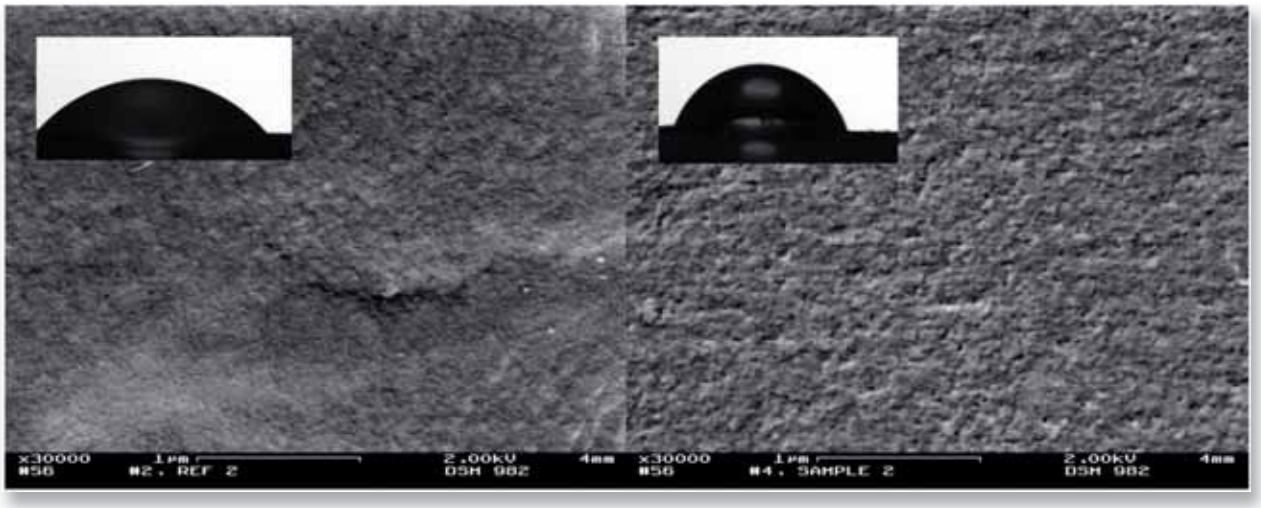

Figure 2. SEM images of pure viscose film (left) and viscose film containing 5 wt-% of lignophenol (right). Inserts show the water droplets set on the film surface, revealing the wetting behaviour of the films.

Solutions containing approximately 95 wt-% of viscose and approximately 5 wt-% of lignophenol were prepared by adding basic aqueous solution of lignophenol into viscose solution by mixing at 150 rpm for 5 minutes using a laboratory stirrer. Blend solutions were evenly spread on the glass plate with the aid of the metal frame to control the layer thickness. The glass plates were immersed into the coagulation bath containing 10% H_2SO_4 to precipitate the solution. Finally, the obtained films were transferred to the distilled water and washed free from salts until the conductivity of the water was <5 μS/cm. The purified films were dried under tension at ambient temperature (20 °C) for 24 h.

The structure of the films was analysed using a SEM, LEO DSM 982 Gemini FEG-SEM and electron energy of 2.0 keV. The film morphology was studied using an XRD, Philips X'Pert MPD diffractometer with Cu X-ray tube (λ=1.542Å). The bulk chemistry was characterised with an FTIR, Bruker Equinox 55 spectrometer and Specac Goleden Gate MK2 ATR accessory with 45° diamond crystal.

Results and discussion

A general view of the fine structure of the precipitated films dried under tension was gained using scanning electron microscopy. In Figure 2, the images of the films prepared using viscose (left) and viscose blended with lignophenol (right) are shown. The lignophenol addition did not impair the film formation, and even structures can be achieved. The inserts in Figure 2 show the water droplets on the film surface, and the small addition of lignophenol seems to increase the hydrophobicity of the films.

Pure viscose films generate the diffractograms of cellulose II showing peaks at 2θ = 12.1°, 19.8° and 22.0°, corresponding to the reflections from (1-10), (110) and (020) planes[2]; see grey line in Figure 3. The black line in Figure 3 is a diffractogram of viscose film to which 5 wt-% of amorphous lignophenol is blended. The crystalline structure of cellulose II is maintained, although the intensity of the reflections is decreased. According to the XRD results, clear changes take place in the intensity curves in the presence of lignophenol. The degree of organisation decreases, and the addition of a small amount of lignophenol leads to a more amorphous film structure. This indicates that attractive cellulose-lignophenol interactions may take place, as the changes in the diffractions patterns are so evident.

Most of lignin model molecules used previously differ in reactivity and size from those of natural lignin[3,4,5]. Until recently, it has been difficult to obtain lignin for interactive studies, with a reasonably high degree of polymerisation that really imitates the effect of polymers. Soluble lignophenol macromolecules are natural polyesters of coumaryl, coniferyl and sinapyl alcohols extracted directly from wood meal with cresol compound and hydrolysed with concentrated sulphuric acid. As a result, a linear α-bonded phenolpolymer with high reactivity is obtained. Based on the results, it seems that lignophenol tends to interact with cellulose, and the even films of regenerated cellulose and lignophenol macromolecules can be achieved.

To confirm the findings, more detailed investigations need to be conducted using, e.g., surface-sensitive methods

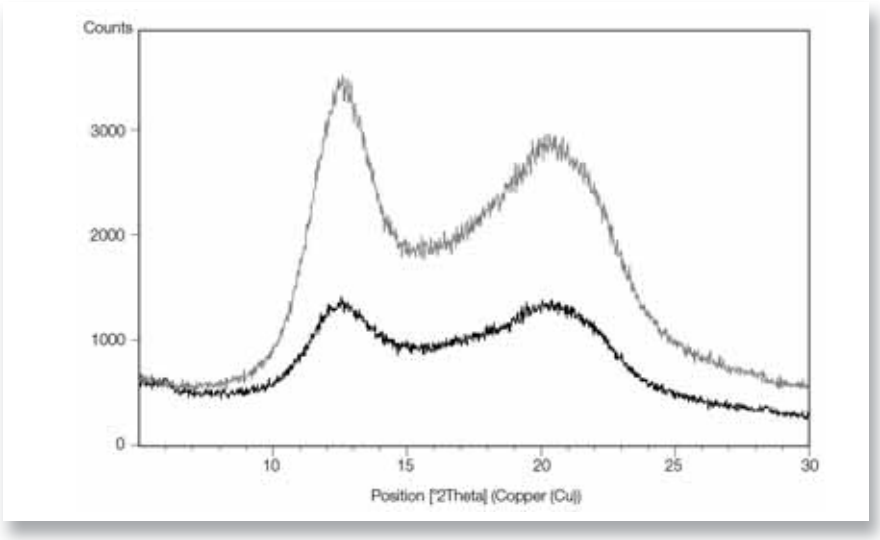

Figure 3. X-Ray diffractograms of viscose (grey line) and viscose film containing 5 wt-% of lignophenol (black line).

such as QCM-D and AFM. We believe that this particular lignophenol derivative facilitates the studying of cellulose-lignin interactions on a molecular level using the aforementioned, sophisticated methods. In addition, more detailed investigations related to changes in the water uptake ability and mechanical properties of the films should be conducted, as lignophenol additions to cellulose fibre composites have shown to give interesting properties such as increased water resistance and strength[6,7].

Conclusions

Even films of cellulose and lignin modelling polymeric lignophenol can be prepared. Hydrophobicity can be increased and the morphology of the films can be altered when reassembling cellulose and lignin modelling derivative from solutions.

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Acknowledgements

EXCELL VTT project group: Risto Hiukka, Vuokko Liukkonen, Unto Tapper and Sirpa Vapaavuori.

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Technical benchmarking of nanofibrillated cellulose compared to commercial polymeric thickeners

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One of the specific advantages of nanofibrillated cellulose (NFC), especially when compared with synthetic thickeners, is its dimensional stability. While synthetic thickeners, polyelectrolytes such as polyacrylic acid and polyvinylpyrollidon, are very sensitive to high temperatures and high salt concentrations, which lead to coiling, rigid nanofibres have the potential to exhibit good thickening performance even under these demanding conditions. A comparative study was therefore initiated of selected NFC qualities of four commercial thickeners. Technical benchmarking of the commercial thickener xanthan gum versus the commercially available NFC, consisting of the viscosity of these different systems, could be measured as a function of shear rate and three different salt contents. The results indicated that xanthan gum is more sensitive to salt addition than fibrillated cellulose is, but that it displays high viscosities at low concentrations.

Materials and methods

Measurements were carried out with the following commercially available thickeners and fibrillated cellulose materials:

Table 1. Materials selected for the study

Thickener	Product name
Polyacrylic acid (PAA)	Aldrich 192058
CMC	Finnfix 700
Polyvinylalcohol (PVA)	Gohsenol GH-23
Xanthan	Keltrol
NFC	Arbocel 100-5

There is a huge number of commercially available thickeners that could be of further interest, but these materials were selected as they were mostly already available at VTT. The materials were dispersed with laboratory mixers and diluted with MilliQ water to target concentrations of 10 and 15 g/l. Sensitivity to salt addition was tested with concentrations of 1 and 6 g/l. Salt was added in the form of sodium chloride (NaCl) and mixed with a spoon directly into a suspension. The total amount of stock solution was 800 ml in a glass beaker, and the measurements were conducted in a 250 ml borosilicate glass beaker. Before the measurements, the pH values and dry matter contents were measured and recorded.

Figure 1. Measurements were performed with a Brookfield RVDV-III+ rheometer and vane spindles. The data were recorded in Rheocalc software.

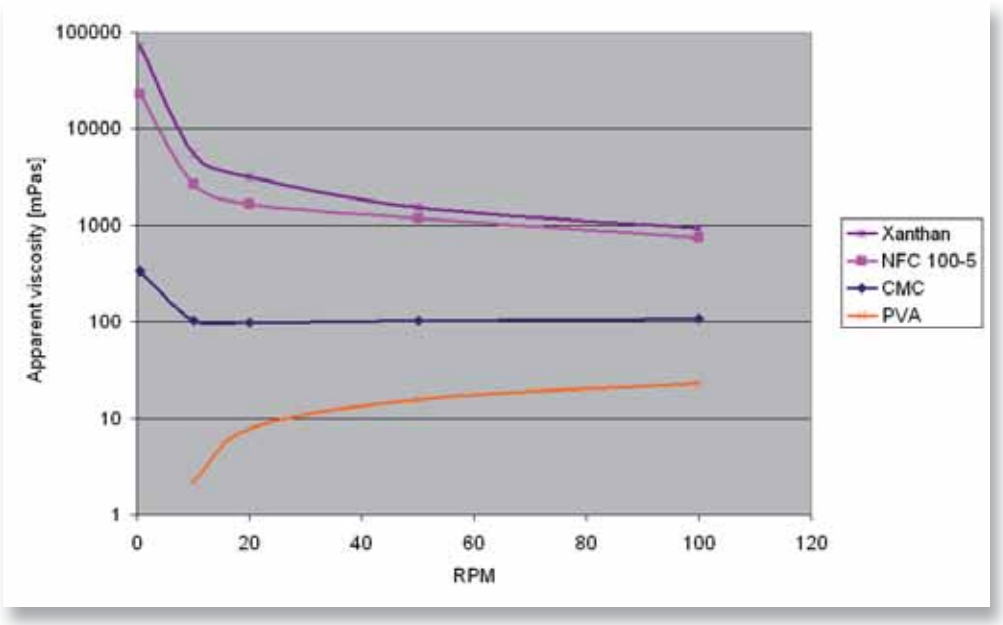

Figure 2. Apparent viscosities of different thickeners in the polymer concentration of 15 g/l without a salt addition. Xanthan and fibrillated cellulose (NFC 100-5) showed shear thinning behaviour.

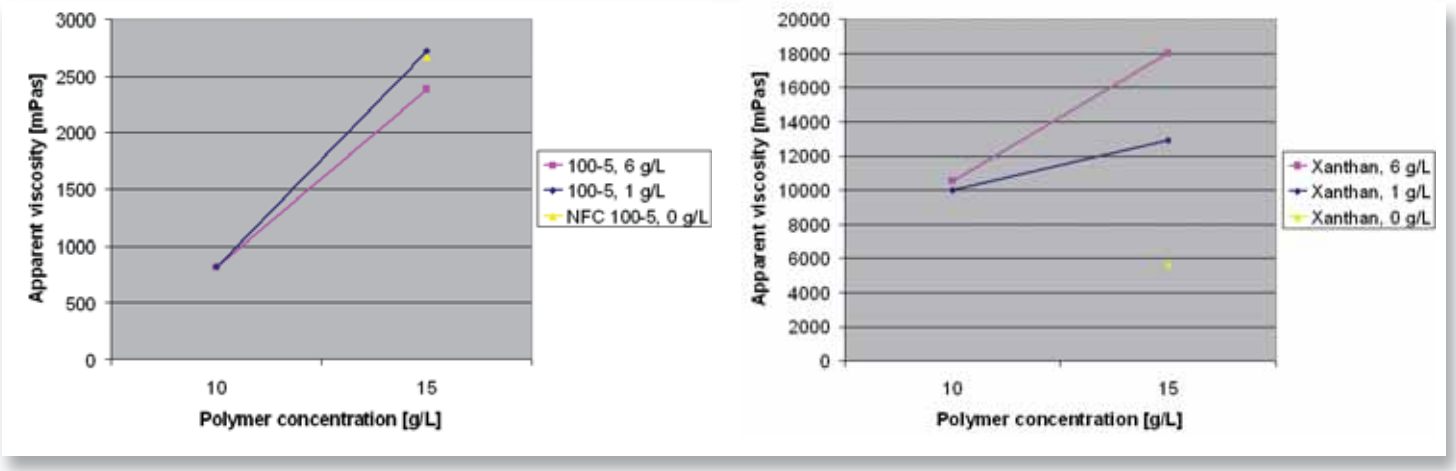

Figure 3. The effect of salt addition on fibrillated cellulose (left) and xanthan gum (right) in different polymer concentrations. The salt additions were 0, 1 and 6 g/l and the rotational speed of the vane spindle was 10 rpm.

Conclusions

The measurements were performed with a Brookfield RVDV-III+ digital rheometer and vane spindles (see figure below). The measurements were recorded in Rheocalc software provided by Brookfield Engineering Laboratories Inc. The rotational speed ranged from 0.5 to 100 rpm, though a more detailed comparison was made at the level of 10 rpm.

Results and discussion

The measurements were started with a polymer concentration of 15 g/l at a pH level of about 6 in order to determine the sensitivity of the Brookfield with the type of vane spindles that were available. It was noted that the sensitivity of the Brookfield was not sufficiently high to measure all the dilute suspensions, as illustrated in the figure below. Polyacrylic acid could not be measured with the existing geometry. The levels of apparent viscosity of 1.5% polyvinyl alcohol and CMC mixtures were too low and the comparison of commercially available thickener and fibrillated cellulose was therefore only performed with Keltrol xanthan gum and Arbocel 100-5.

The results indicated that xanthan is much more sensitive to salt addition than fibrillated cellulose Arbocel 100-5 at the limited range of polymer concentrations. The effect was higher when the polymer concentration was 15 g/l. The viscosity of xanthan increased notably with added salt, but the fibrillated cellulose remained more stable. Only a slight decrease in viscosity was observed at a polymer concentration of 15 g/l, presumably resulting from a slight decrease in flock size and structure.

Xanthan and NFC both showed shear thinning behaviour. The reason for the change in viscosity of xanthan was probably mainly due to a conformation transition of the molecule and electrostatic forces. A coiling phenomenon due to increased salt concentrations at these dosage levels, similar to that of many other thickeners, did not seem to occur. It is more likely that the molecules straightened and formed an ordered network of stiff molecules. This phenomenon could not be studied in detail during this project, however, but has been studied in numerous international publications.

The dimensional stability of NFC could be an advantage for industrial applications in which fibrillated cellulose can be used as an industrial processing aid. A further comparative study of other commercially available and new NFC grades would be of high fundamental interest, especially to test the thickening performance of fibrillated cellulose materials. Arbocel 100-5 was not the only NFC available. It was noted that there is room for more outstanding NFC grades as, at low concentrations, commercially available products like xanthan display unusually high viscosities, which are important to their suspension-stabilising properties.

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CCA – Carbamated cellulosic derivative

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Carbamate cellulose (CCA) is introduced with a novel synthesis technique for biomaterials. The CCA invention has been released previously at VTT, but now the focus is on improved synthesis and a dissolution technique especially for fibre manufacturing.

Background

The manufacture of fibres and films from cellulose by the viscose process has been known about for more than a hundred years. Even today, almost all cellulose-based fibres are manufactured by the viscose method. It is a known method by which various properties of the final product are achieved by varying the material and process parameters. The viscose method has significant drawbacks, however: the preparation of the spinning solution includes laborious work stages, and the carbon disulphide used for the dissolution is toxic, inflammable and combustible, and difficult to recover. Furthermore, some of the carbon disulphide decomposes into hydrogen sulphide, which is also toxic and explosive. In addition, the viscose solution is an unstable product, which means that it cannot be stored as an intermediate product, and all the steps of manufacture must be taken without delay from beginning to the end, keeping the mass at a low temperature.

There have been several known attempts to replace the viscose method with a more ecological method. The most promising one has been the conversion of cellulose into cellulose carbamate by means of urea (see, for example, D. Klemm et al., Comprehensive Cellulose Chemistry, Wiley-VCH 1998). In spite of its obvious advantages and several known attempts, this method has remained on a laboratory scale however. The reasons have included problems with the homogeneity of the product, the recovery and residues of the organic auxiliary agents (e.g., hydrocarbon) and/or solvents (normally ammonia) used, the properties of the final products (primarily fibres), which have been no more than satisfactory, and the operational costs of the methods developed.

Known attempts to provide a method for manufacturing cellulose carbamate have been based on the soaking of pulp sheets in an alkaline solution (mercerization), which, in some cases, has included an addition of ammonia and/or other solvents or accelerators. After mercerization, the pulp, which has been partly dried by compression, is treated in a urea solution, which may include the addition of an alkalizing agent, and usually also ammonia and possible solvents or salts. Finally, the reaction between the urea and the pulp is carried out in an oven at a temperature of about 130°C. The methods have required the best viscose cellulose with a DP level that has been reduced by, for example, long-term curing in a mercerization solution or irradiation in advance. Examples of the above-described processes are presented in patents FI 61033, EP 0 402 606 and WO 00/08060.

One of the first attempts to manufacture cellulose carbamate is presented in U.S. Pat. No. 2,134,825. It uses the aqueous solution of urea and sodium hydroxide, with which the pulp sheets are first impregnated. After the impregnation, settling and compression, the mass is dried and heated in the oven to achieve a reaction between the cellulose and the urea. The patent presents a number of chemicals to improve absorption and reduce the gelling tendency of the solution. This patent also presents the use of hydrogen peroxide for the purpose of reducing the viscosity of the solution. Pulps manufactured on the basis of the patent have also only been partly soluble in such a way that a large quantity of unreacted fibres is left in the solution, jamming the spinning nozzle. This is probably due to the unevenness of the substitution.

In all known methods for manufacturing cellulose carbamate, an alkaline solution (aqueous sodium hydroxide) is used to activate (swelling) the pulp, as in conventional mercerization of pulp. An exception to this, U.S. Pat. No. 2,134,825, experiments with the use of hydrogen peroxide, with and without sodium hydroxide, to activate the pulp for the purpose of reducing the vis-

cosity of the solution. VTT's patents FI-20020163, FI-20030027 and, for example, its related US patent 7,662,953, present a novel approach in which typical plastics mixing and processing equipment are used for carbamation synthesis. No pre-mercerization or other activation is needed, and processing is carried out in an unforeseen dry state. In this study, the above-mentioned CCA technique is further developed and tested for a special grade of cellulose and for a fibre-spinning application. The aim is to increase the cellulose content while simultaneously keeping the high solution quality. This way, the fibre properties and overall process economy are improved.

Aims

The aim of the current effort was to fulfil the requirements of the cellulose fibre-spinning industry. This concerns mainly the strength of the fibre. A further aim was to increase the cellulose content of the spinning solution. This is supposed to increase the strength of the fibre, and it will also improve the overall process economy. More specifically, the target fibre properties are

- Fibre fines (titre) ~ 1.7 dtex
- Dry strength > 1.9 cN/dtex

In this study, the starting dissolved cellulose was cotton (or linter). It is generally known that cotton (linter) is a much more complex starting cellulose for the viscose process, and it is assumed that this also holds for the CCA technique. It is contradictory to make fibre from cotton using a wet-spinning technique, however, as cotton is in itself a good fibre without transformation. This may be explained in two ways: 1) we are concerned with the linter (i.e., non-fibrous residual of cotton material) and 2) the price of cotton is competitive with wood-based cellulose due to local subventions.

Materials and methods

The CCA synthesis is executed as described in above-mentioned patents. The key process parameters that were varied were urea feeding, moisture content, passes through the mechanical compacting device, oven time and temperature.

The CCA dissolution technique also has various parameters by which it is possible to affect the quality of the solution. Now, the target is to increase the cellulose content as much as possible. Essential parameters are pre-wetting of mass, a mixing strategy and the mixing blade configuration. Chilling of the mass during all the phases is also important.

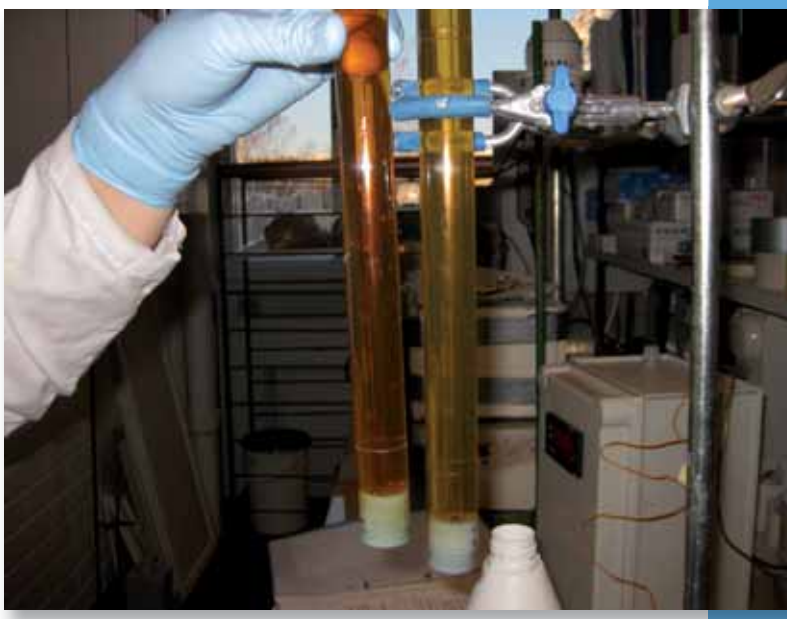

Figure 1. Dissolution sample from wood-based (right) and cotton-based (left) cellulose.

Results and Conclusions

The processing of cotton-based cellulose was very challenging. Numerous recipes and dissolution configurations were studied before the above-mentioned targets were reached. The key to success was, surprisingly, in the dissolution phase. During the work, a novel multiphase dissolution technique was developed. There is a patent application on the process for this technique. Figure 1 shows a dissolution example from the cotton solution and related wood-based solution.

Publications

Patent application for the multi-phase dissolution technique

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Tailoring of nanocellulosic materials for industrial applications

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The forest industry is looking for new technological solutions and products. One very interesting opportunity is the production and use of cellulose nanofibres for new types of materials and novel applications. Nanocellulosic materials are expected to have their first application areas within paper industry products. One of the aims is to create new application and product openings outside the paper sector, which requires the creation of novel, cross-disciplinary scientific knowledge on fundamental material characteristics as well as on chemical and biotechnical modifications of nanocellulose fibres. These are the main aims of the public cross-disciplinarily project called Tailoring of Nanocellulosic Materials for Industrial Applications (Naseva) run jointly by TKK, VTT and nine industrial partners.

The work in the project can be divided into three main areas: a) to modify the surface of nanocellulose by different means with the goal of enhancing the applicability of nanocellulose materials in new products, b) to understand the interactions between modified nanocellulose and other substances on a molecular level and c) to evaluate the suitability of the modified nanocellulose in various applications, such as composites, nanomaterial additives and porous materials. In this paper, the application of nanocellulose as a nanoparticle-dispersing additive, biochemical modification and some aspects of the safety of nanocellulose will be presented as examples of VTT's research topics in the project.

Nanofibrillated cellulose as a carrier of nanoparticles

Inorganic nanoparticles have recently been incorporated into clear coating systems to improve targeted properties such as the scratch or UV resistance of the coatings[1,2] . For example, the addition of inorganic nanoparticles, typically silica or aluminium oxide, to organic coatings can result in a strong increase in scratch and abrasion resistance. Many metal oxides are also known to absorb UV radiation; the most common of these is zinc oxide (ZnO).

To obtain the improved properties, the nanoparticles need to form a homogeneous dispersion, combined with good stability during storage and drying of the coating[4]. The difficulty of dispersing nanoparticles and integrating them into systems has limited the commercialisation of nanoparticle-enabled products, however, as the potential of nanoparticles cannot be fully utilised. In addition, relatively high amounts of the nanoparticles are needed in order to obtain the desired properties.

In this project, we have studied the potential of nanofibrillated cellulose as an additive that stabilises the inorganic nano- or microparticle additives used in transparent coatings.

Figure 1. Distribution of solid microparticles in the lacquer matrix without NFC (left) and with NFC (right).

Figure 2. Colour changes of coated pine wood samples after 308 hours of exposure to UV light. Left: lacquer containing inorganic nanoparticles; right: lacquer containing NFC and inorganic nanoparticles.

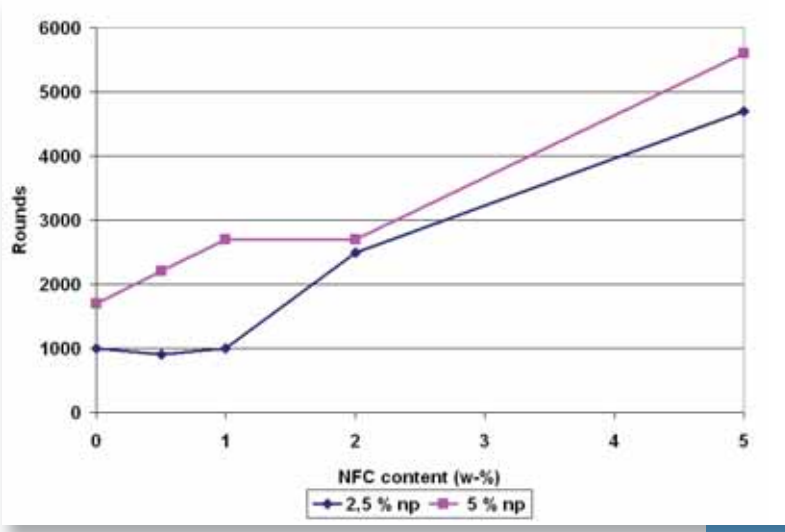

Figure 3. Effect of NFC amounts on abrasion resistance. Amount of nanoparticles 2.5 or 5 w-% from the solids content of the lacquer.

Results and discussion

Nano/microparticles were evenly dispersed into the matrix when NFC was used, whereas the particle matrix without an NFC addition deposited them at the bottom (Figure 1). The mixtures remained stable for more than one month. During this time, some separation of the particles could be seen, but after a little shaking, the particles were once again evenly distributed in the lacquer matrix.

With the addition of NFC to the lacquer, the consistency of the mixtures can be adjusted over a wide range of viscosities. Shear thinning behaviour is generally proportional to the amount of NFC added. During 20 days of storage at room temperature, the viscosity of the mixtures containing NFC did not change.

NFC had no observable disturbing effect on the film formation of the lacquer mixtures. The drying was monitored visually on the glass plates and all the surfaces were dry within two hours, similar to the surface of the reference lacquer. The film remained transparent.

UV protection of wood with transparent coatings is challenging. The colour and natural appearance of wood used for interior applications such as furniture, decorative panels, joinery, etc. are often desired, and wood is protected with transparent systems. The addition of colourless UV light absorbers in clear finishes has only found moderate success however.[3]

Based on our results, the addition of NFC clearly improves UV durability of the wood substrate coated with inorganic nanoparticles containing lacquer; see Figure 2. When NFC was used as an additive, the inorganic nanoparticles were uniformly distributed in the lacquer matrix, and the dispersion was stable. This ensured an even distribution of particles on the sample surface and thereby improved UV durability. For UV durability, amounts below 0.5 w-% of NFC (calculated from the solids content of the lacquer) are sufficient to stabilise the inorganic particles. The improvement was dependent on the nanoparticle type and amount.

Our results showed that NFC improves the abrasion resistance of lacquer containing silica nanoparticle dispersion; see Figure 3. The abrasion resistance increased with the amount of NFC. The adhesion between different coating layers was also improved with NFC. The coatings used today, for example, on high-abrasion resistant wooden floors, contain higher amounts of nanoparticle additives than used in this study.

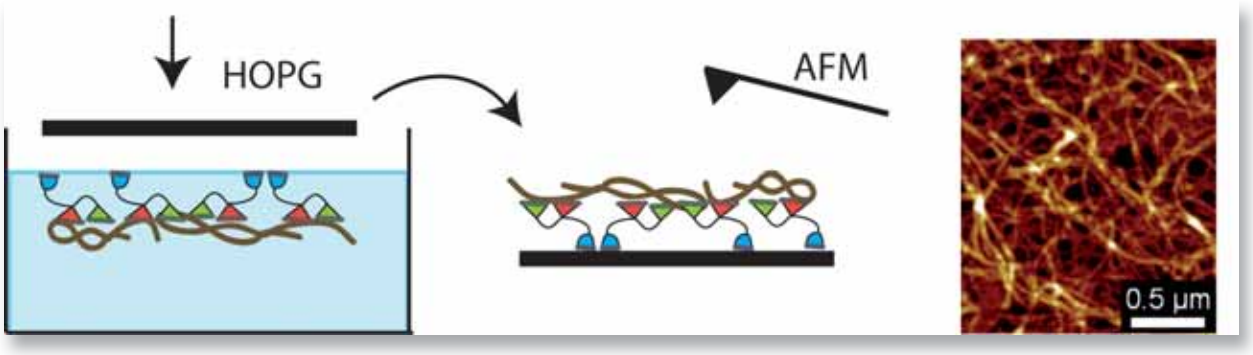

Figure 4. a: A schematic presentation of self-assembly of NFC (brown ribbons) functionalised by the HFBI-DCBD protein. Hydrophobin pointing away from the water is presented as blue parts, whereas red and green triangles mark the cellulose binding domains. b: The film could be transferred onto a hydrophobic surface for AFM investigation. c: A resulting AFM image.

Conclusions

Nanofibrillated cellulose acted as a synergistic additive in the coating application. Besides being a rheology modifier, NFC properties can be used as a dispersion-stabilising additive for solid or dispersed particles in coating applications[5,6]. The addition of NFC to inorganic nanoparticles containing lacquer clearly improves the UV durability and abrasion-resistance properties of dry lacquer coating. UV durability and scratch resistance are both surface phenomena. UV light cannot penetrate deeper than 75 µm and visible light no deeper than 200 µm into wood surfaces[7]. As the nano/microparticles are evenly distributed in the coating surface, their properties can be fully utilised for improving the UV durability and scratch resistance of the coating.

Our results indicate that properties such as scratch resistance, UV stabilisation, anti-microbial activity and conductivity/anti-static properties can be integrated into coatings with the aid of nanoparticles carried by NFC.

Biochemical modification of NFC by a cellulose-binding hydrophobin fusion protein

The modification of nanocellulose can be achieved in many ways. Our approach was to use biochemical interactions in the surface modification of nanofibrillar cellulose (NFC) and cellulose nanowhiskers. Biochemical modification allows for the addition of functions in mild conditions by supramolecular assembly of molecules, avoiding chemical alterations such as bond breakage, thus maintaining the nanofibrils in as native a state as possible.

HFBI-DCBD fusion protein

For the modification of NFC, a fusion protein containing two cellulose binding domains (CBDs) and a hydrophobin protein was chosen. The protein has two functional sites, one has an affinity for nanocellulose and the other is very amphiphilic. Thus, the decoration of NFC by the fusion protein was assumed to bring surface activity to the NFC fibrils.

Properties of HFBI-DCBD-functionalised NFC

After modification by the hydrophobin fusion protein, the NFC fibrils were able to assemble at air/water and oil/water interfaces. A scheme of the way interfacial layers were formed and investigated is presented in Figure 4. Functionalised NFC was allowed to adsorb at the air/water interface. This resulted in a hierarchical film in which the hydrophobic parts of the hydrophobins faced the air. The whole film was then picked up on a hydrophobic solid surface and analysed by atomic force microscopy. The resulting films were thin and consisted of a mesh of cellulose nanofibrils. Similar films could also be formed from cellulose nanowhiskers. In situ studies of interfacial tension and interfacial rheology confirmed the formation of very elastic films[8].

Encapsulation of oil droplets and nanoparticles by functionalised NFC

NFC functionalised by biomolecules was an efficient emulsion stabiliser. The NFC itself was able to encapsulate large oil droplets, but in the presence of the HFBI-DCBD proteins, it could form highly stable emulsions containing oil droplets with a diameter of about a hun-

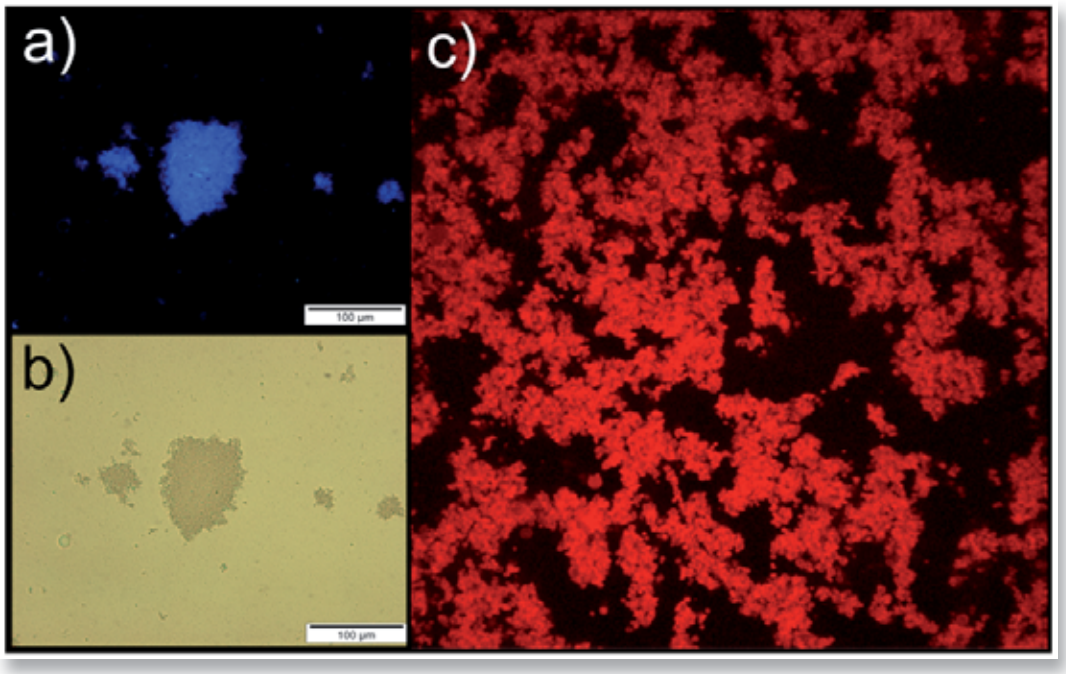

Figure 5. Emulsions stabilised with NFC and HFBI-DCBD. An epifluorescence (a) and a bright field, (b) image of emulsion containing nanodroplets associated into larger agglomerates. In Figure a, cellulose has been stained with Calcofluor. c: A confocal microscopy image of an emulsion in which the oil phase has been stained with Nile Red. Image size 128 × 128 µm.

dred nanometres. Examples of emulsions stabilised by functionalised NFC are presented in Figure 5. The small oil droplets were associated with the NFC matrix, which provided good stabilisation of the emulsion by supporting the oil droplets and preventing separation of the phases. The emulsions were stable for several months.

The NFC and the HFBI-DCBD fusion protein could also provide long-term stabilisation of nanoparticles. We showed that nanoparticles, which would normally be unstable and tend to aggregate, remained nanosized when they were fixed to the NFC matrix by the fusion protein. The most striking difference was observed during storage of the nanoparticle suspensions in high ionic strengths mimicking physiological conditions. It is essential that the formation of emulsions and nanoparticle dispersions remain stable during the storage and processing steps when designing drug and food formulations.

Safety aspects of nanocellulose

Health, safety and environmental issues of nanomaterials have recently raised many concerns. In this study, we evaluated the worker exposures to nanoparticles in air during the production of nanocellulose. We also exposed mouse macrophages and human monocyte-derived macrophages to nanocellulose *in vitro* and studied the viability and cytokine profile of the cells thereafter (study carried out at the Finnish Institute of Occupational Health). We also studied the ecotoxicological effects of nanocellulose using the kinetic luminescent bacteria test with *Vibrio fischeri*.

Results

The processing of nanocellulose did not cause significant exposure to particles during normal operation. The grinding generated a small amount of particles, which were mostly removed by a fume hood. The potential for particle release from the spray-drying operation occurred at the moments when the process was opened or the end product was handled, i.e., opening of the end product container and the spray dryer, and packing the end product. Only low amounts of airborne particles were detected however[9].

No evidence of inflammatory effects or cytotoxicity on mouse and human macrophages was observed after exposure to nanocellulose. The results of the toxicity studies suggest that nanocellulose is not cytotoxic and does not have any effects on the inflammatory system in macrophages.

From an ecotoxicological point of view, the tested nanocellulose concentrations were very high compared with the concentration traditionally assumed environmentally harmful. Nanocellulose was not acutely toxic to *Vibrio fischeri*, however, in environmentally relevant concentrations.

ACKNOWLEDGEMENTS

The Naseva project was funded by Tekes (Finnish Funding Agency for Technology and Innovation) and a project consortium:

- Research partners: VTT and Aalto University
- Industrial partners: UPM, Ahlstrom, Carlsberg, Dynea, Elastopoli, Glykos, Kareline, Nokia, Teknos

Special acknowledgements go to the VTT scientist mentioned in this summary article and many other coworkers not mentioned here.

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Improvement of composite properties by nano-sized birch bark

Antti Nurmi, Kirsi Immonen

The aim of the project was to use fine-powdered, suberin-rich outer birch bark to improve the elasticity and flexibility properties of gypsum board and multiple properties of wood fibre bioplastic composites. In Finland, the approximated annual consumption of birch wood is about 17 Mm^3, generating 1.1 Mt of bark and, finally, 0.16 Mt of suberin-rich outer bark[1]. Bark goes into energy production, but the new proposed waste act classifies bark as a by-product that should primarily be used in next-generation production and not for energy production.

Indroduction

Earlier research at VTT indicates that chemically modified reactive birch bark suberin can be used in novel adhesives and coatings[2]. The aim of this project was to investigate if micronized birch bark particles can create extra properties when mixed with mineral-based binding agents (cement-based plaster, gypsum) or biopolymers (PLA, PHB) in composites. For instance, PLA and PHB are both brittle, and PHB is susceptible to water absorption. Improvements of these properties are needed to extend the use of biopolymers.

The project was divided into three parts:

Task 1. Comparing different milling and fractionating techniques and their ability to create fine particles.

Task 2. The effect of birch bark on improving elasticity and other properties of cement and gypsum when mixed in small quantities.

Task 3. Investigating if micronized birch bark can improve the properties of biopolymers (PLA and PHB) as well as the cross-linking ability of biopolymers and cellulose fibre in composites.

Materials and methods

Dried birch bark was first milled with a hammer mill and then fractionated by sieving. The brittle inner bark was ground into very small particles and it could easily be separated from the bigger flakes with more elastic outer bark. The fractionated outer bark was then milled using different techniques in order to minimize the particle size. The techniques were spray milling (Hosokawa Alpine) in the dry phase, pearl milling (Hosokawa Alpine AHM90) in the aqueous phase and finally fluidisation (Fluidiser M-110Y) of the spray-milled fractions (circulation 14 times: pressure variation 200-1300 bar, chamber

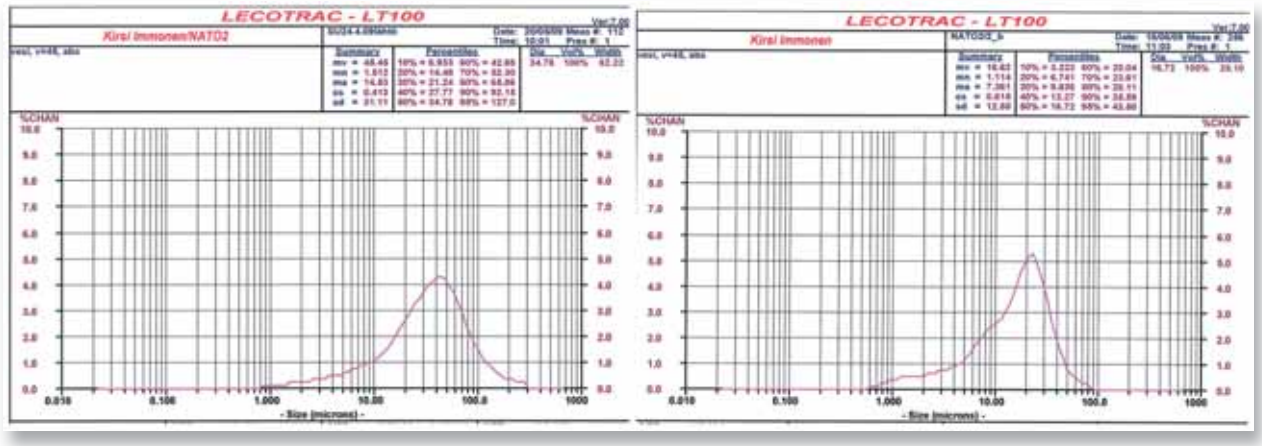

Figure 1. Particle size distribution of spray-milled birch bark (left) and fluidised birch bark (right).

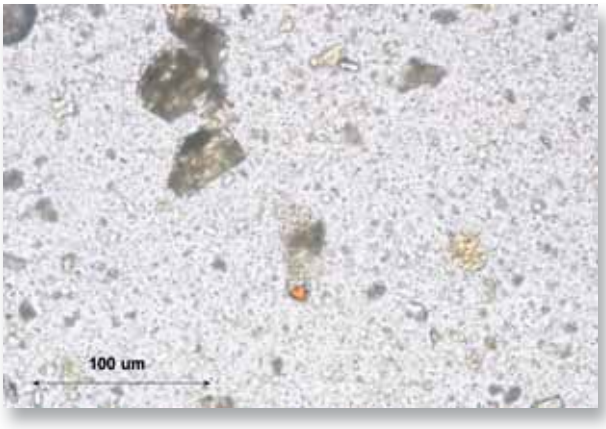

Figure 2. Microscopic image of a spray-milled sample taken from the filter.

size 400-100 µm). The distribution of particle size was measured to compare the milling techniques using the particle size analyser Lecotrac LT-100.

Between 1% and 20% (m/m) of the spray-milled birch bark was mixed with gypsum and cement plaster. The dry materials were homogenised before adding the water. In the case of the polymer spray, the milled birch bark was compounded with pure polymers and with polymers together with 20% and 30% birch pulp or CTMP. The compounds were produced by a twin-screw extruder, and the test bars were injection moulded with the Engel ES 200/50HL injection moulding machine.

Results and discussion

Particle sizes

The particle size distribution of spray-milled and fluidised birch bark is given in Figure 1 and the microscopic image in Figure 2. Spray milling resulted in particles with an average size of 40 µm, and further fluidisation decreased the average particle size to 20 µm. Further grinding of the spray-milled bark with a pearl mill had a positive effect on the particle size. In general, the grinding of birch bark was found to be quite difficult because of the high content of wax components. To achieve a particle size close to nano-scale requires a large amount of extra energy. Alternatively, new techniques should be explored.

Birch bark together with mineral binders

The results showed that in the case of the gypsum matrix with fine particles of birch bark (spray-milled << 200 µm), the modulus of elasticity increased with increasing bark content. This means that birch bark made the matrices more elastic. The same tendency was found with cement plaster. The addition of bark had a negative effect on the bending and compression strength for both matrices however. In the case of wet-ground, small bark particles, the negative effect seemed to be smaller and, for instance, the compression strength of gypsum increased when 5% of wet-ground bark was added.

Birch-bark containing biopolymer composites

The main results are given in Table 1. The addition of birch bark (≤ 5%) clearly improved the flexibility of polylactic acid (PLA) by 100% from 15.3 kJ/m^2 to 31 kJ/m^2. The other important improvement was a 40% decrease in water absorption of polyhydroxybutyrate (PHB) with a birch bark addition of less than 5%.

Table 1. Overview of the effect of birch bark on the properties of biopolymers.

Polymer	Tensile	Stress strain	Charpy impact	Water abs.
PLA	-	++	++	+ / -
PLA + MAH	--	+	+	-
PHB	+ / -	-	-	++
TPS	+ / -	--	--	+ / -
PP	+ / -	--	--	not tested

Further studies were carried out with composites containing biopolymers (PLA and PHB), birch pulp or CTMP, and fluidised birch bark. The most important fact was to study whether suberin-rich birch bark is able to cross-link biopolymers and cellulose fibres during composite processing. The results for these fibre-containing compounds are presented in Figures 4, 5 and 6.

The results in Figure 4 for PLA- fibre compounds showed no improvements in tensile strength due to birch bark in the birch-pulp containing samples but a small improvement in the CTMP-containing sample with fluidised birch bark. For the PHB fibre samples in Figure 5, the tensile strength results showed a small increase when fluidised birch bark was used. This indicates that the small birch bark could be milled; some clear improvements in tensile strength could be found.

The assessment of impact strength properties in Figure 6 showed an improvement of 60% in impact resistance in fluidised birch-bark containing PLA samples with 20% birch pulp compared with pure PLA-cellulose compound. It was also found in the DSC results that the presence

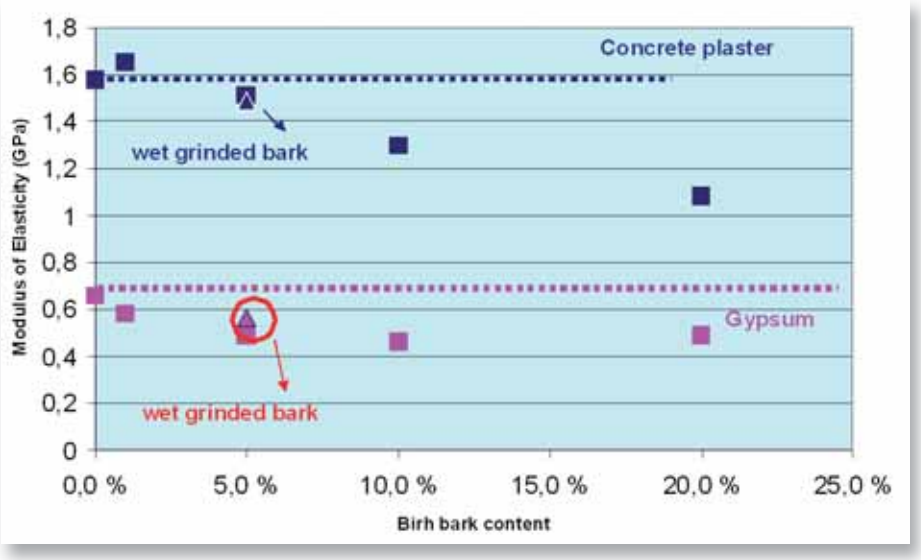

Figure 3. Effect of birch bark content on the modulus of elasticity of gypsum and cement plaster.

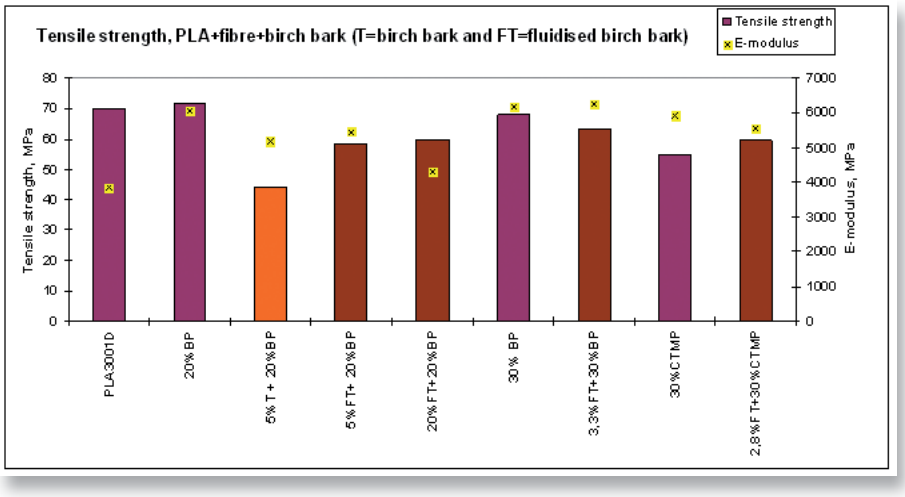

Figure 4. Tensile strength of PLA-cellulose fibre compounds with and without birch bark additive.

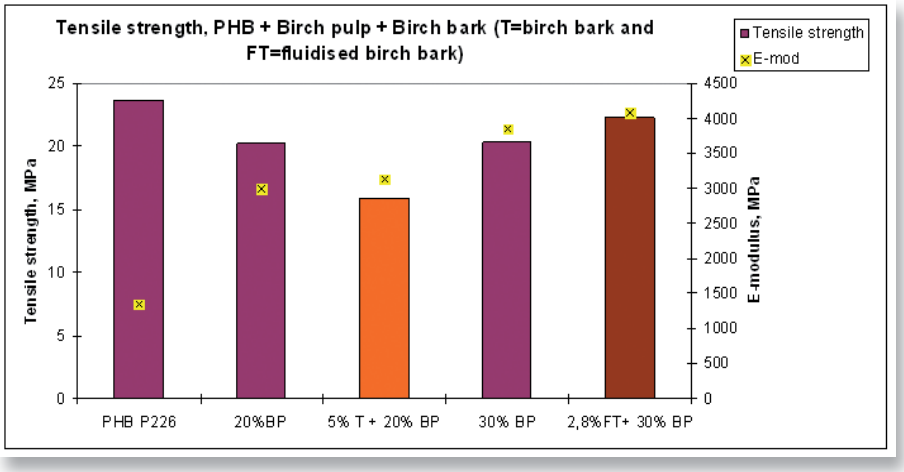

Figure 5. Tensile strength of PHB-cellulose fibre compounds with and without birch bark additive.

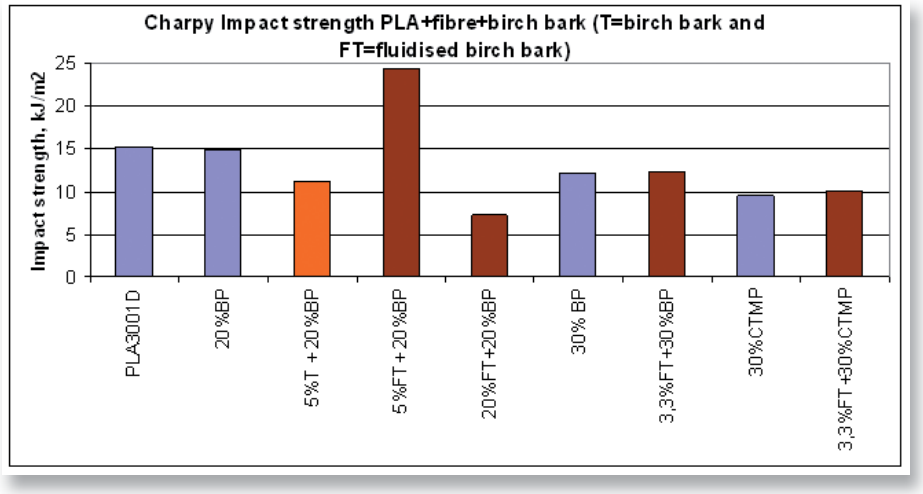

Figure 6. Impact strength of PLA-cellulose fibre compounds with and without birch bark additive.

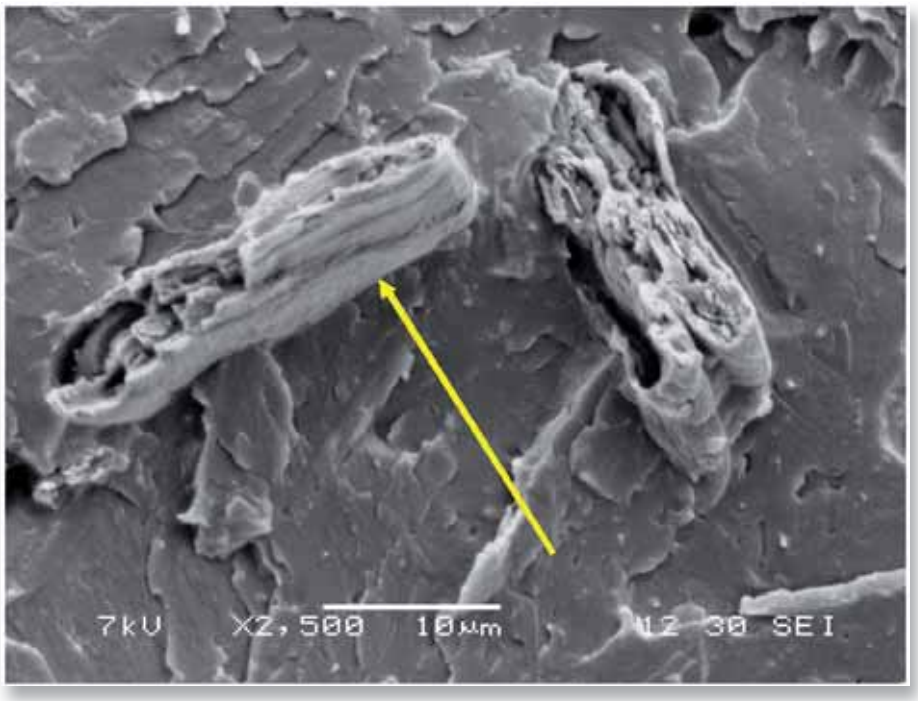

Figure 7. Micrograph of composite-containing PLA, birch pulp and 20% birch bark.

of birch bark inhibits crystallisation of PLA in processing. Figure 7 shows that there is no gap between the polymer and the cellulose. Moreover, in Figure 8, clear bridges can be seen between the PLA and birch pulp. Similar kinds of bridges were also found in the case of PHB plus birch pulp. Results from the DSC showed clear changes in melting and crystallisation behaviour of PLA with the presence of birch bark. These findings could not be proved by FTIR or C13 NMR studies however. Nevertheless, in the FTIR spectra, a clear widening of the ester peak (~1760) and new peaks (1084, 869, 756) were noticed.

Conclusions

This study with birch bark as an additive in cement, gypsum and biocomposites resulted in several promising improvements. Powdered outer birch bark to a particle size of less than 20 µm improves the flexibility properties of the mineral-based matrix. More significant improvements were found when fluidised bark was added to the PLA and PHB matrix. A small addition of birch bark to PLA resulted in a 100% improvement in impact resistance and an increase in elongation while maintaining the tensile toughness of PLA. In addition, the clear decrease in water absorption of PHB is a very positive outcome.

Figure 8. Clear bridges between PLA and birch pulp in the presence of birch bark (3.3%).

PLA-birch pulp samples with a fluidised birch bark addition resulted in a 60% increase in impact strength. In fibre-containing samples, the preliminary spectroscopic studies did not verify the cross-linking between the cellulose and polymer matrix. he microscopic findings and the enhanced properties of composites indicate that micronized birch bark has an effect on the compatibility of cellulose in the biopolymer matrix. There was also a clear indication that the smaller particle size had a stronger effect on composite properties, which can lead to the conclusion that pure suberin may also be effective as a biocomposite additive.

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Expanded plastics – Trends and technologies

Kalle Nättinen, Tero Malm, Kyösti Valta

Technologies, potential applications and commercialisation routes for the production of expanded plastics and, in particular, bioplastics were surveyed. The motivation for the production of expanded materials arises from the following needs: savings in material costs by reducing the density of the materials (Figure 1), reductions in energy consumption in transportation through weight savings in vehicle structures and the legislative pressure to produce materials with high insulation potential. The possibility of producing a material that fills one or more of these needs with green materials is an attractive added prospect.

Materials and methods

There are two main routes for obtaining expanded structures: chemical and physical expansion. Chemical expansion is based on blowing agents that produce gases through their thermal decomposition during processing. The process is limited to relatively high resulting densities, but it can easily be implemented in existing equipment without modifications. The physical foaming methods are based on either particle expansion (e.g., EPS), in which granules or pellets of plastics are impregnated with expansion agent such as pentane, CO_2, etc. and subsequently expanded in a batch or a continuous process, or a continuous process in which the expansion agent (e.g., $scCO_2$) is fed into the polymer melt in a separate compounder or, alternatively, using a single extruder combined with a static mixer.

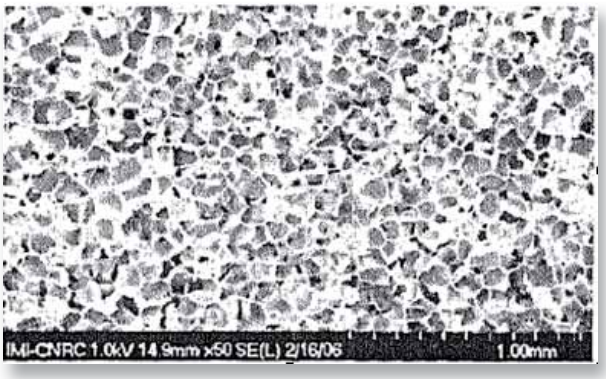

Figure 1. Expanded PLA with a density of 33kg/m^3. [1]

Results and discussion

The benefits of physical expansion include capacity for the production of very low densities (<50 kg/m^3) and the use of inexpensive foaming agents such as N_2 and CO_2. The (commercial) downsides are the investment costs related to the modification of equipment.

Conclusions

Expanded materials are already a multi-billion dollar business. The successful application of expansion technologies to bio-based materials is expected to increase the business potential further through the synergy of the materials and the energy savings combined with the neutral or, at least low, carbon footprint of bio-based plastics as starting materials.

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Crosslinking as an efficient tool for decreasing moisture sensitivity of biobased nanocomposite films

Jari Vartiainen, Ali Harlin

Chitosan-nanoclay bio-hybrid films were successfully crosslinked with glutaraldehyde, genipin and glyoxal. The moisture sensitivity of the films decreased as a result of crosslinking, leading to improved barrier properties against water vapour and oxygen. Chitosan films containing both genipin and nanoclay had a water vapour transmission rate of 72 g×100µm/(m²×24h), which was 34% lower than for pure chitosan and 30% lower than for chitosan/nanoclay without crosslinkers. Glyoxal-induced crosslinking resulted in a 92% reduction in the oxygen transmission rate at 80% relative humidity compared with pure chitosan films. Oxygen transmission through glyoxal-treated chitosan/nanoclay film was 2.8 cm³×100µm/(m²×24h), which was 53% lower than for chitosan/nanoclay without crosslinkers. Nanoclay and, especially, glyoxal crosslinking also reduced water vapour sorption of chitosan considerably. Crosslinking may be used as an efficient tool for enhancing the exploitability of naturally hydrophilic biopolymers towards new high-value applications, such as food packaging.

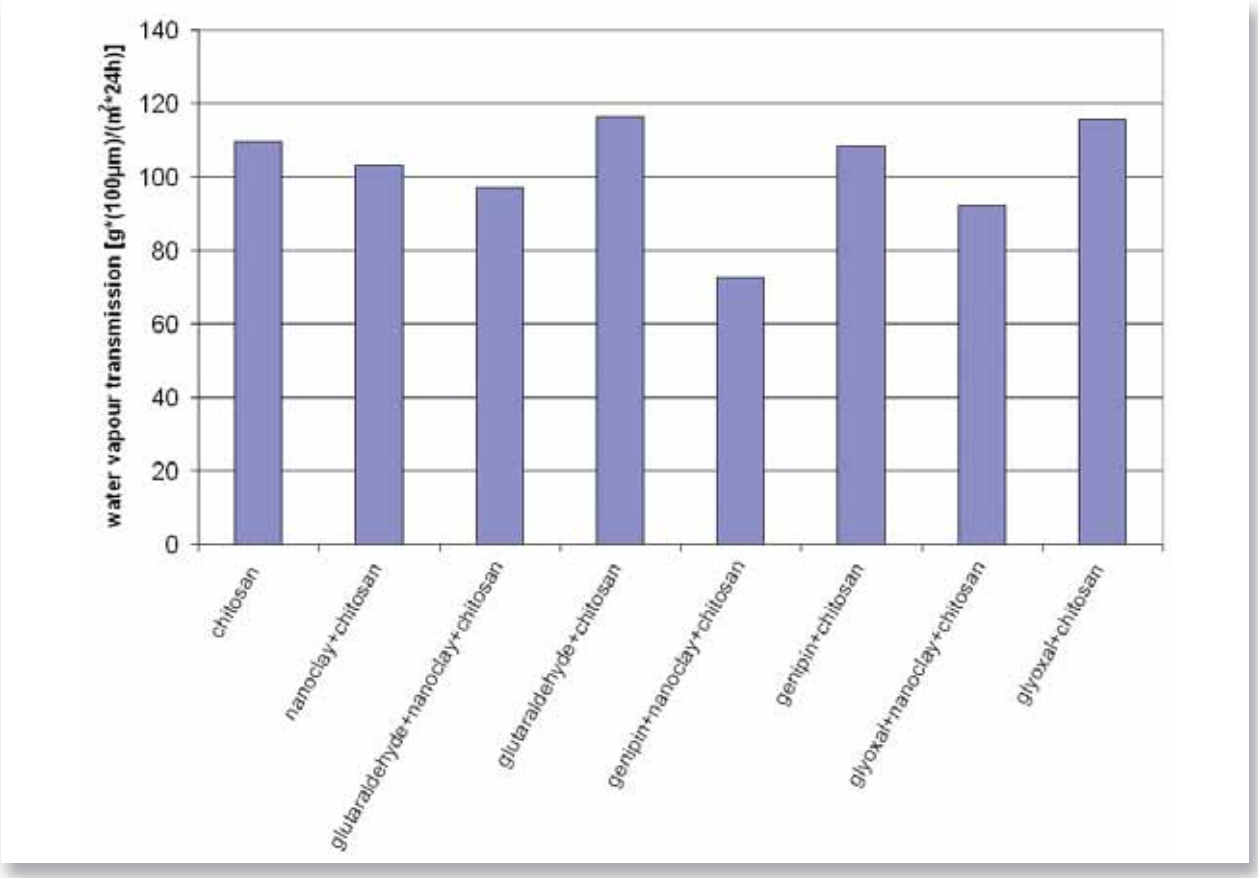

Figure 1. Water vapour transmission rate of glutaraldehyde, genipin and glyoxal-crosslinked chitosan-nanoclay films (measured at 100/50% RH).

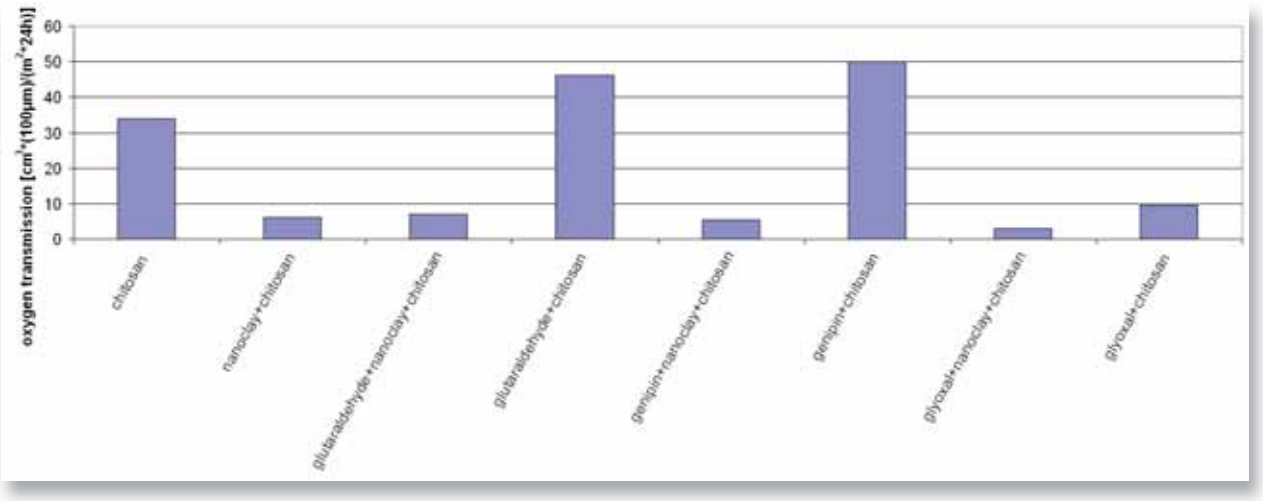

Figure 2. Oxygen transmission rate of glutaraldehyde, genipin and glyoxal-crosslinked chitosan-nanoclay films (measured at 80% RH).

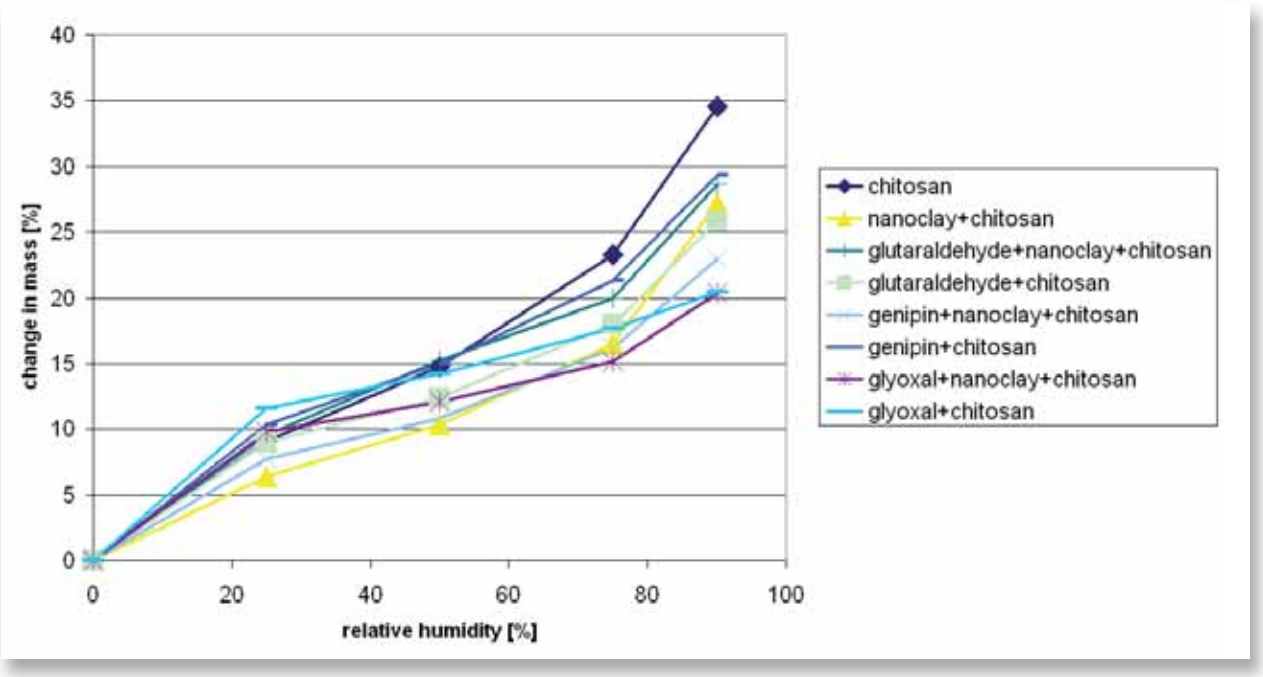

Figure 3. Water vapour sorption of glutaraldehyde, genipin and glyoxal-crosslinked chitosan-nanoclay films.

Materials and methods

Nanoclay (montmorillonite) was dispersed into chitosan solution using sonification. Crosslinkers (glutaraldehyde, genipin or glyoxal) were dissolved in ethanol and added under rigorous mixing. Films were cast onto polystyrene Petri dishes and dried at room temperature. The water vapour and oxygen transmission, as well as water vapour sorption, were determined.

Results and discussion

As the water vapour transmission results indicated, nanoclay improved the barrier properties of chitosan films (Figure 1). Crosslinking did not provide any protection against water penetration, however, except when used in combination with nanoclay. Chitosan films with genipin and nanoclay had water vapour transmission rates of 72 g×100µm/(m²×24h), which was 34% lower than for

Figure 4. Completely transparent glyoxal-crosslinked chitosan-nanoclay film.

pure chitosan and 30% lower for chitosan/nanoclay without crosslinkers. Crosslinking prevents humidity-induced swelling of chitosan, which reduces the diffusion of water molecules. Barrier improvements due to nanoclays are explained using the tortuous path theory, which relates to the alignment of the nanoclay platelets. As a result of crosslinking and intercalation, the effective path length for molecular diffusion increases and the path becomes highly tortuous to reduce the effect of gas and moisture transmission through the film.

Chitosan and other biopolymers with a crystalline structure and hydrogen bonds are typically very good oxygen barriers but only up to 50% relative humidity. In high humidity conditions, water molecules penetrate between the chitosan chains and destroy the hydrogen-bonded structure and barrier properties. Nanoclay clearly improved the oxygen barrier properties at 80% relative humidity (Figure 2). Crosslinking only improved the barrier properties when applied together with nanoclay however. Glyoxal-induced crosslinking of chitosan/nanoclay films resulted in a 92% reduction in the oxygen transmission rate compared with pure chitosan films. The oxygen transmission through glyoxal-treated chitosan/nanoclay films was 2.8 $cm^3 \times 100\mu m/(m^2 \times 24h)$, which is 53% lower than for chitosan/nanoclay films without crosslinkers.

Biopolymers, such as chitosan, have a high natural affinity to water, thus films without nanoclay or crosslinkers absorbed almost 35% of the water at 90% relative humidity. Nanoclay and, especially, glyoxal crosslinking, prevented sorption considerably (Figure 3). Nanoclay without crosslinkers provided the lowest absorption at low humidities, whereas glyoxal-linked chitosan performed better at high humidities. These results are consistent with both water vapour and oxygen barrier improvements. The absorbed water molecules weaken the intermolecular interactions, such as hydrogen bonding and crystallinity, leading to reduced barrier properties. Nanoclay and crosslinking prevented water solubility and swelling of chitosan, which increased the number of silicate layers per unit volume, eventually resulting in low permeability.

Conclusions

Chitosan-nanoclay bio-hybrid films were successfully crosslinked with glutaraldehyde, genipin and glyoxal. The moisture sensitivity of the films decreased as a result of crosslinking, leading to improved barrier properties against water vapour and oxygen. Crosslinking may be used as an effective tool to enhance the exploitability of naturally hydrophilic biopolymers towards new high-value applications, such as food packaging.

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Pressure-loss measurements of fibre pulp at high consistency

Jarmo Kouko

Conventional paper and board manufacturing with forming consistencies over 4% is difficult or impossible because of the problems of web forming. The maximum consistencies of fibre suspensions that can be pumped with MC pumps are about 18-20%. Piston pumps with line pressures over 200 bars allow much denser fluids to be pumped. The key idea of forming with high-consistency pulp is energy savings at all stages of the processing, i.e., during refining, pumping and forming of the pulp, as well as during drying of the formed object. In this case, the formed object will not be paper; instead it may be thick board-like web. The web or object has to have some adequate strength properties, though there is less need for other normally important properties such as formation, brightness, printability, etc. of conventional papermaking.

Materials and methods

During this project, a method and a device were developed to measure the pressure loss of a fibre-water suspension at high consistency in pipe flow. The tests were performed with a slow-speed test rig that was designed for VTT's plunger moulding press tester (Figure 1). Pressure loss can be transformed into viscosity or apparent viscosity, which is a key parameter in the design of flow channels and forming dies. The studied pulp was unrefined pine pulp (CSF 680 ml, length-weighted average length of fibre 2.3 mm).

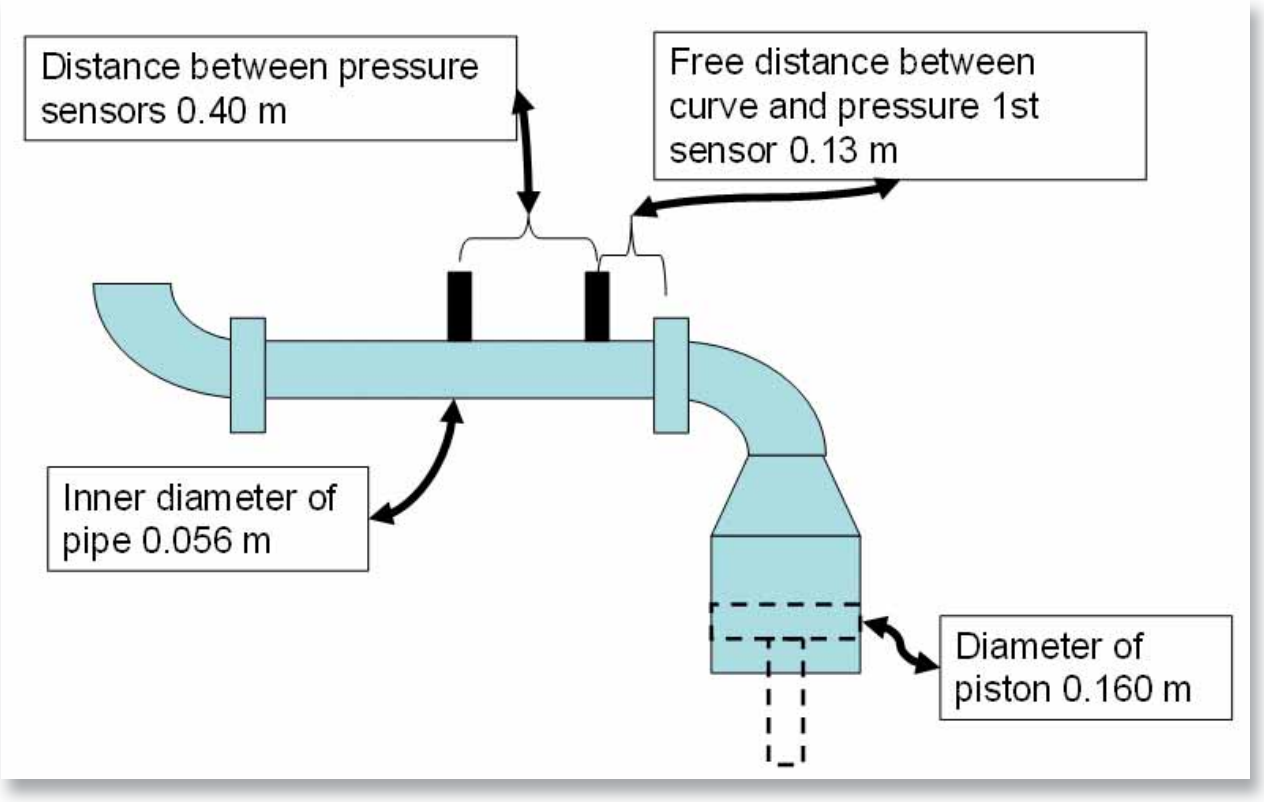

Figure 1. Schematic presentation of the test rig that was inserted into VTT's plunger moulding press.

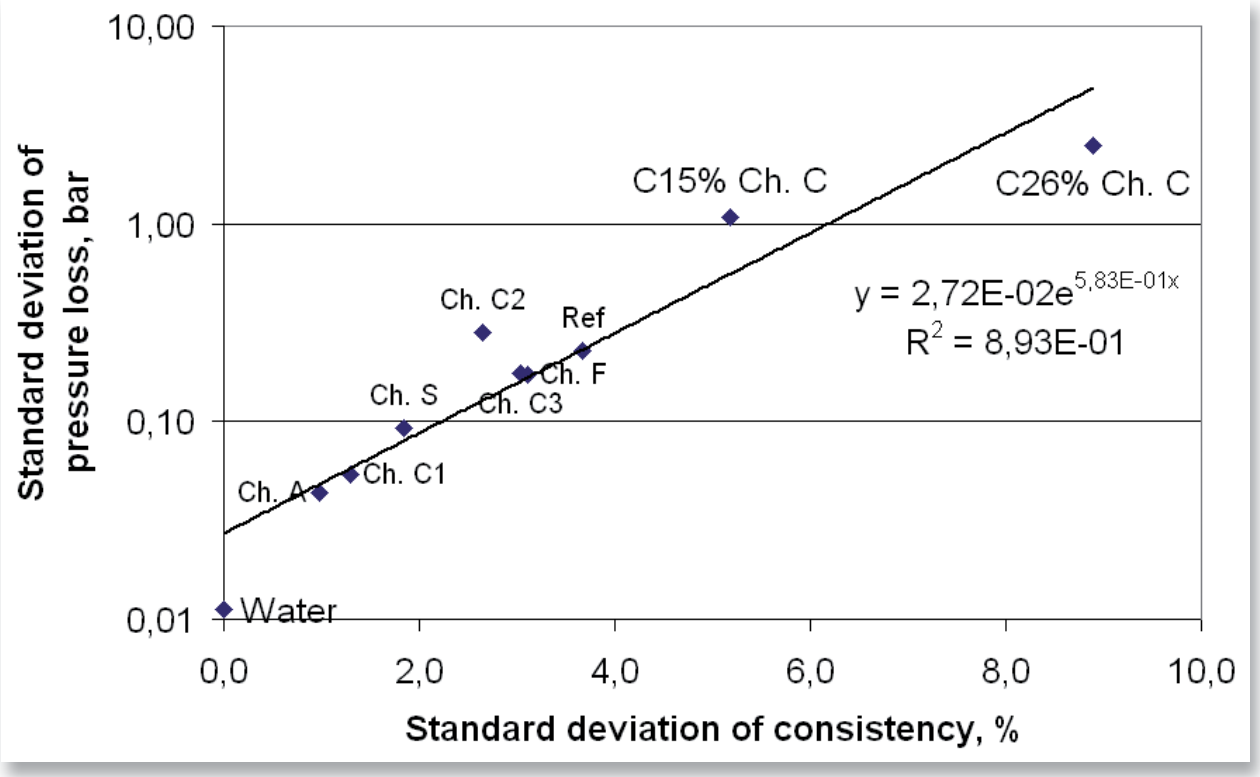

Figure 2. Standard deviation of consistency vs. standard deviation of pressure loss.

According to literature[1,2], the anionic charge and high molecular weight of the chemical promotes fluidization of suspensions. There are other known possibilities to reduce apparent viscosity, e.g., boundary-layer injection and gas injection to a suspension. Some anionic chemicals were therefore selected for these trials in order to reduce the pressure loss (apparent viscosity) of the pulp suspensions in the pipe flow.

Results and discussion

The viscosity of the pulp suspensions varied between 0.7 and 180 mPas, and the consistency of the pulp varied between 0 and 26%. Most of the tests were performed on pulp with a consistency of 6.5%. There was a strong correlation between the consistency and the viscosity of the fibre-water suspension in the pipe flow. The deviation of the viscosity of the suspension in the pipe flow comes from the deviation in consistency, which is a consequence of the separation of fibres and water. Bends and contractions in a pipeline promote the separation of fibres and water. By adding a fluidizer chemical, the average viscosity can be lowered. Chemicals can also be used to control consistency and prevent variations in consistency (Figure 2). The fluidizer acts as a dispersion chemical and lowers the internal friction (viscosity) of the fluid. When the optimal amount of chemical is used, the deviation of viscosity is probably much smaller than in these tests. The accuracy of the pressure measurement in this project was not optimal but good enough to show the viscosity range of pulp at different consistencies.

Conclusions

The most important finding in this project was that the deviation of the viscosity of the suspension in the pipe flow comes from the deviation in consistency, which is a consequence of the separation of fibres and water. By adding fluidizer chemicals, it is possible to control the consistency and reduce the variation in consistency.

For further studies, an improved tester machine will be needed in which higher consistencies and higher volumes of pulp can be formed into objects. As a result of this project, some important technical requirements for further studies have been recognized:

- Dewatering of pulp to a high consistency
- Mixing of chemicals to pulp at a high consistency
- Construction of an improved tester
- Functional and measurement options in the improved tester
- Geometry of a possible forming die
- Measurement of pressure loss

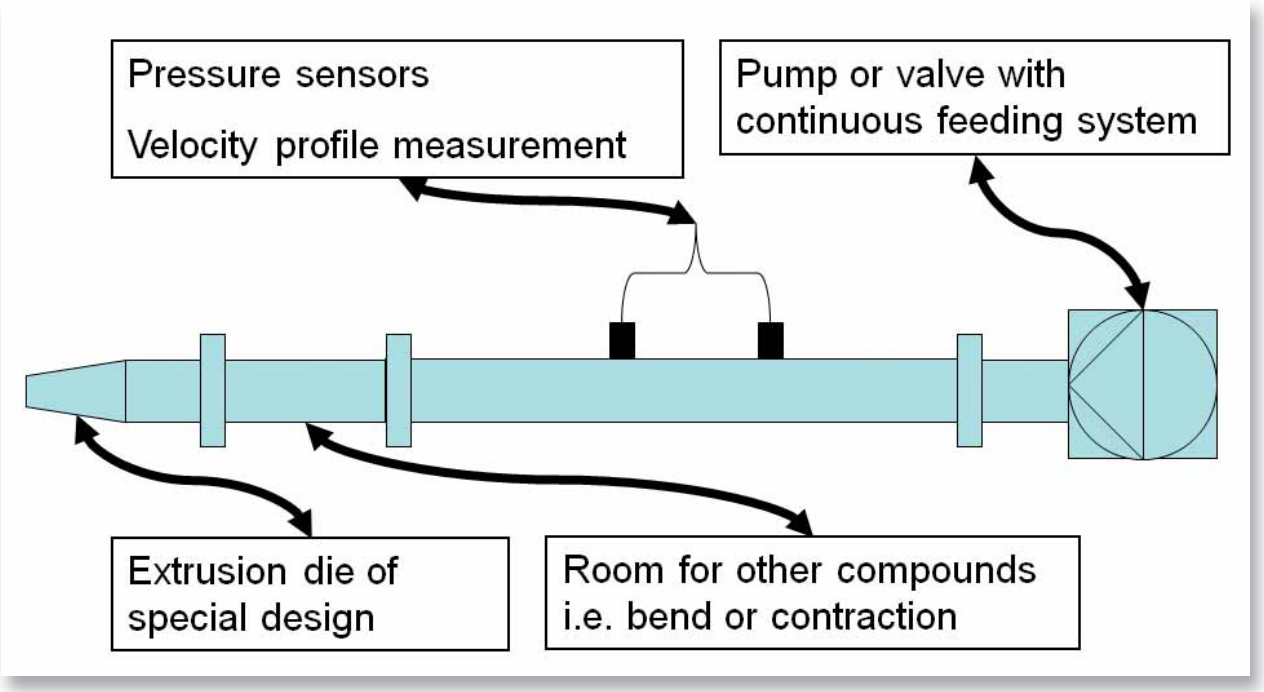

Figure 3. Schematic presentation of the next improved tester for extrusion of pulp at high and ultra-high consistencies.

A schematic presentation of the improved tester for high-consistency pulp is shown in Figure 3.

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A novel method for improving cellulose functionality in specific applications

Kirsi Immonen, Anne Kallioinen, Kyösti Valta, Eino Sivonen, Matti Siika-Aho

The aim of this study was to find out if mechano-chemical dry processing method could intensify production process or enhance product quality as pre-treatment method for further enzymatic or chemical processing. The study was divided into several tasks. The first task was to find out if combined mechano-chemical and enzymatic processing could lead to better alkaline solubility of cellulose carbamate made with the dry processing method. In the second task, mechano-chemical pre-treatment was applied to enhance the enzymatic total hydrolysis of lignocellulosic biomass. The third task was to employ the mechano-chemical dry processing method for CMC pre-treatment for different modification purposes such as control of the polymerisation degree (DP) and compaction of CMC.

This study showed a possibility not only of dry processing methods using VTT's own compacting technology but also of combined enzymatic and dry processing methods. As soon as the dry material content of cellulose-enzymatic processing can be increased to a level >50%, these two methods together can offer new environmentally friendly processing options for several cellulose modification processes. The new compacting method can already be used as a low solvent and energy-saving process method. Besides cellulose, this method can also be applied to several other biomass processes.

Introduction

Cost-effective, energy-efficient and environmentally friendly production methods are sought in the development of new technologies that use renewable resources for energy production and for the conversion of lignocellulosic material into new products. Bioconversion of lignocellulosic biomass into ethanol and other valuable products has been under investigation for decades. The area has recently attracted growing interest, and large-scale production trials have been launched. In the production of ethanol and other chemicals from biomass, one way is to produce sugars first by enzymatic hydrolysis and then to continue with further processing. Enzymatic modification of cellulose has also been found to be an option for increasing the alkaline solubility of dissolving pulp and replacing the conventional viscose process, which contains toxic chemicals. The method, aimed at controlled degradation of cellulose by endoglucanase enzymes, was developed in the EU project Biocelsol. This project studied the same idea for improving the alkaline solubility of cellulose carbamate by partial enzymatic hydrolysis. If the solubility of cellulose in alkaline solutions increases, it may be possible to decrease the amount of alkali.

To enhance the enzymatic activity in lignocellulosic material modification, different kinds of chemical and mechanical pre-treatment methods have been developed. In this project, the aim was to study the dry modification method combined with chemical treatment in very low chemical amounts using a dry compactor. The dry modification method (e-compactor) is modified using pelletizing equipment, which can be used as novel pre-treatment technology for several kinds of organic materials. It is based on VTT's own technology with a patent application in December 2010[1]. Compared with existing solvent-phase technologies, it can save energy and solvents, making it more environmentally suitable as a pre-treatment for different lignocellulosic fibre modifications. Compared with existing pelletizing methods, this equipment configuration also allows natural material compaction with significantly less friction heat formation than commercial equipment.

The task of this project was to apply the dry modification method for cellulose-containing fibrous material to improve the activity in the hydrolysis process and enhance reactivity for enzymatic derivatisation. Cellulose fibres have shown a strong ability to break and fibrillate during the dry compacting process with dry material contents above 30%. In enzymatic hydrolysis with lignin-containing materials, the lignin retards the reaction. By break-

Figure 1. The laboratory-scale compactor with a new roller-plate construction.

ing down and fibrillating the fibre surfaces, the cellulose is more accessible for enzymatic hydrolysis and chemical modification towards cellulose derivatives. The dry modification/compacting method enables the addition of chemicals that can modify and solubilise lignin or ingredients activating the cellulose surface together with the fibre surface breaking process. Raw materials such as dissolving pulp, mechanical mass, spruce chips, cellulose carbamate, CMC and reed canary grass were tested for different purposes.

Materials and methods

Dry modification using the e-compactor

Lignocellulosic material is usually modified using methods with high water content, allowing fibre separation when mechanical energy and shearing forces are introduced into the system. The high water or solution content needs several processing steps before the actual goal of modification is achieved however. Residual water and solvents are also often problem wastes that need to be purified or disposed of. One solution to this problem is to use dry modification methods or very low solvent content modification methods. These are mainly different physical modifications such as different milling methods, plasma or corona modifications, or vapour or heat treatments.

In dry compacting/pelletizing with commercial equipment, some materials are known to easily block the material flow by creating a material wedge in front of the rollers. This prevents free rotation of the rollers and generates excess friction between the material and the pan plate, and it thus starts to burn the material. The phenomenon quickly dries the material and the problem becomes dynamically worse. Finally, the compacting process must be halted and the pan plate cleaned by drilling or some other time-consuming method.

In VTT's own technology-based compacting device, a new modified configuration is used for compounding, mixing and homogenising bio-based material systems with significantly less friction. The compactor creates local and transient high pressure, shear and elongational deformations to the material system together with a high temperature gradient. This could generate and also maintain useful chemical reactions. Thus, we call it a reactive compounding system or e-compactor (Figure 1).

Enzymatic treatments for enhanced alkaline solubility

The process to treat pulp for enhanced alkaline solubility was divided into two different parts: the enzymatic treatment before or after carbamation, which was made using dry compacting method. The method developed by VTT for the alkaline-soluble cellulose carbamate process is documented more thoroughly in patent US 7,662,953 and patent application US 20090283717, and the process is based on the use of urea in carbamation. On the other hand, it is known that it is possible to introduce alkali into cellulose modified by enzymatic treatments. This is presented in the EU project BioCelSol. The aim of this testing procedure was to find out if these two techniques combined would give an even better quality, yield and economy than the separate techniques on their own.

The process for alkaline solubilisation, according to these two methods, was as follows:

1. **Enzymatic treatments** for dissolving pulps (Domsjö and Borregaard) -> **carbamation** using the dry compacting method with urea (and peroxide) in a dry material content of 68% -> washing with water -> testing of alkaline solubility.
2. **Carbamation** of dissolving pulp (170604 and Linters) using the dry compacting method with urea (and

Table 1. Raw materials for enzymatic treatments.

Cellulose	Additional Information	Dry weight (%)
Cellulose carbamate (CCA)	17.06.04; Dp 305, Nitrogen 1.95	96.7
Cellulose carbamate (CCA)	Linters: Dp 190	98.5
Dissolving pulp	Domsjö Fabriker (never- dried pulp)	20.3
Dissolving pulp	Borregaard,16.3.2010 (T)	95.6

Table 2. Raw material pretreatments.

Lignocellulose	Chemicals	Mechanical treatment	Dry weight after pretreatment (%)
TMP	25% NaOH	5xE-comp.	34
	5% Na-persulfate	10xE-comp.	38
	5% H_2O_2 +cobalt	10xE-comp.	35
	5% H_2O_2	10xE-comp.	34
	10% H_2SO_4	5xE-comp.	30
	-	-	31
	-	10xE-comp.	34
Spruce chips	-	-	40
	-	10xE-comp.	46
	5% H_2O_2 +cobalt	10xE-comp.	39
	25% NaOH	10xE-comp.	45
Reed canary grass	-	-	52
	-	10xE-comp.	67

peroxide) in a dry material content of 68% -> e-compactor treatment -> drying and reacting in oven -> washing with water -> pressing to a dry material content of 40% -> **enzymatic treatments** -> testing of alkaline solubility.

Enzymatic treatment was carried out for two dissolving pulps (Domsjö and Borregaard) and two cellulose carbamates prepared according to process procedure 2 (Table 1). The dissolving pulp from Domsjö Fabriker was a reference sample from the Bifocals project to check that the enzyme hydrolysis worked properly. Enzymatic hydrolysis was carried out with commercial endoglucanase obtained from AB Enzymes Finland. Enzyme treatment was carried out at a temperature of 50°C with a pH of 5 at 5% consistency dry material content for 3 hours. The enzyme dosage was 500 nkat/g cellulose. The reference treatment was carried out similarly but without the enzyme. The release of dissolved sugars during the enzymatic treatment was analysed with the DNS method[3].

The alkaline solubility of samples was analysed by dissolving cellulose samples in 9% NaOH solution at a temperature of -5ºC followed by separating and weighing the alkaline-insoluble fraction.

Total hydrolysis of lignocellulose

Chemical and mechanical treatments were carried out with the e-compactor. Chemicals were added to the raw materials (Table 2) by spraying chemicals onto the raw material batch in Kahl-type mixing vessel. The materials were then mechanically treated or compacted using the e-compactor. The particle size of the material was decreased, the material surface was fibrillated and, at the same time, the material was warmed up from room temperature to max 50°C. Before enzymatic hydrolysis, the materials were washed with hot water to remove chemicals and all soluble material, and filtered with a Büchner funnel.

The enzymatic hydrolysability of the washed solid fraction was analysed at 1% dry material content in test tubes with magnetic stirring at a temperature of 45°C. The commercial cellulase mixture Celluclast 1.5L FG (Novozymes) and β-glucosidase Novozym 188 were used for enzymatic total hydrolysis. The enzyme dosage was 10 FPU/g dry matter for cellulase and 100 nkat/g dry matter for β-glucosidase. Hydrolyses were carried out and the remaining solids were removed by centrifugation. The reducing sugars released in the enzymatic hydrolysis were monitored using the DNS method[3].

The carbohydrate composition of pretreated, washed, raw materials was analysed by total acid hydrolysis from selected samples[4]. Resulting monosaccharides were analysed using high performance anion exchange chromatography (HPAEC-PAD)[5].

CMC pre-treatments

These CMC treatments were conducted after discussions with customers to find out if there was any indication that the mechano-chemical treatment using the e-compactor could be possible for their purposes and form a basis for customer projects.

1. DP control for the CMC product

Raw material CMC with a dry material content of 57% was obtained from the customer. First, it was dried in an oven to a dry material content of 82%. Next, the CMC was treated by spraying it with a catalyst water solution and then with hydrogen peroxide. This moist mixture was compacted a few times with an e-compactor and sent to the customer for further testing of the viscosity and DP level. Enzymatic treatment was used as a reference for this mechano-chemical treatment.

2. Compacting trial for CMC

The CMC grade specified by the customer was compacted with the e-compactor from a few very high dry material contents >55% with and without starch additives. In the last test with the lowest dry material content, the CMC was run through a blade mill after compacting.

Results and discussion

Effect of enzymatic treatments on the enhanced alkaline solubility of cellulose carbamate

Cellulose carbamate is made using mechano-chemical methods and dry compacting with the e-compactor. The

Table 3. Effects of enzymatic treatments on the cellulose yield and alkaline solubility.

Cellulose	**Treatment** (g cellulose for treatment)	**Solubilised sugars** (% of dry weight)	**Total yield loss** (% of dry weight)	**Alkaline soluble cellulose** (%) / (quick test*)
CCA 17.06.04	reference (3g)	< 0.1	-	85.6
CCA 17.06.04	enzyme (3g)	2.4	-	94.4
CCA 17.06.04	enzyme (132g)	2.0	20.9	- (soluble)
CCA Linters	reference (3g)	< 0.1	-	99.4
CCA Linters	enzyme (3g)	3.3	-	100
CCA Linters	enzyme (110g)	2.8	4.6	- (soluble)
Dissolving pulp Borregaard	reference (3g)	< 0.1	-	-
Dissolving pulp Borregaard	enzyme (3g)	2.4	-	-
Dissolving pulp Borregaard	enzyme (328g)	2.0	2.0	- (soluble)
Dissolving pulp Domsjö	reference (3g)	< 0.1	-	-
Dissolving pulp Domsjö	enzyme (3g)	2.8	-	-

* Quick was the test performed just to see the solubility, without weighing the amount of residues

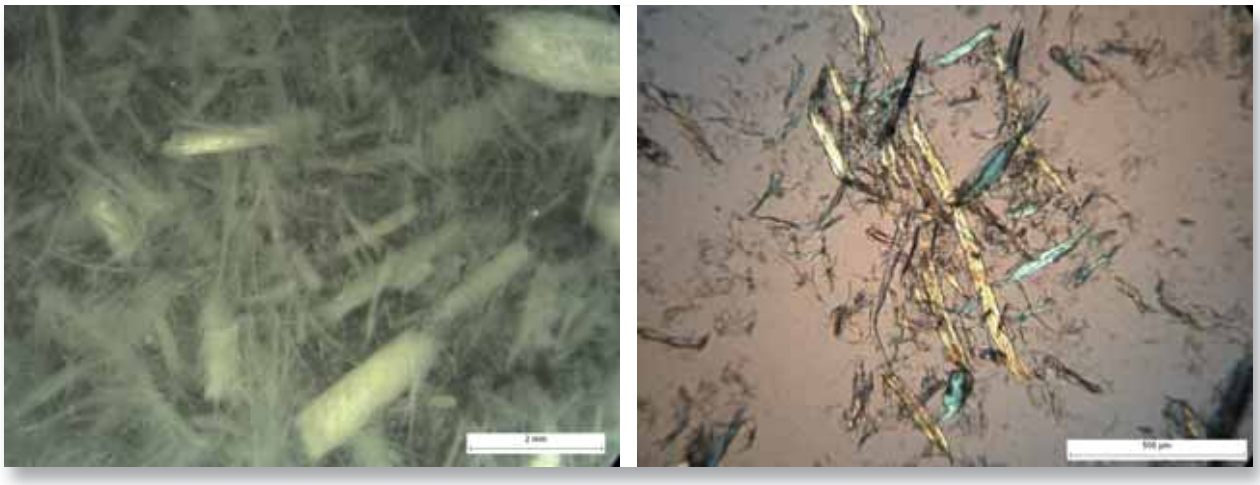

Figure 2. The effect of e-compactor treatment on spruce chips before (left picture) and after ten treatment cycles (right picture).

purpose of this study was to find out if enzymatic treatment before or after the carbamate process could enhance the alkaline solubility of cellulose carbamate. Two different ready-made cellulose carbamates and dissolving pulps were treated enzymatically for 3 hours at 50°C, pH 5. After the treatment procedure presented in the methods, the extent of hydrolysis was analysed by analysing the dissolved sugars from the treatment water (Table 3).

According to Table 3, about 2-3% of the original cellulose was solubilised and detected as reducing sugars after the enzymatic treatment, whereas in the reference treatments without enzymes, solubilisation did not occur. In larger-scale treatments, the solubilisation of sugars was lower than in the smaller 3g treatments. The total yield loss was analysed from the larger-scale treatments. For Borregaard-dissolving pulp, the total yield loss was similar to the solubilised sugars, but for both of the cellulose carbamates, the total yield loss was higher than the sugar loss, especially for CCA 17.06.04. The total yield loss might have been higher due to the solubilised oligosaccharides or other compounds. The structure of cellulose carbamate has probably partly degraded during the enzymatic treatment. The alkaline solubility of cellulose carbamate 17.06.04 was increased by enzymatic treatment, but part of the material remained insoluble with the studied method.

These results showed that a small increase in alkaline solubility can be achieved using enzymatic treatment combined with the carbamate process. The biggest problem with this procedure is that carbamation is performed using dry methods (water content <50%) and enzyme treatment has to be carried out with a high water content (water content >95%). From the processing point of view, it was not very cost-effective, however, with regard to the results obtained.

Effect of chemical and mechanical treatments on enzymatic hydrolysability

The effect of mechano-chemical pre-treatments on the enzymatic hydrolysability of biomass aimed at the ethanol process was studied. Mechano-chemically pre-treated (Table 2) and washed materials were enzymatically hydrolysed for 48 hours (or 72 hours), and the sugars released during the hydrolysis were analysed from the samples. The effect of the e-compactor treatment on the fibre can be seen best in the spruce chips. Figure 2 presents the spruce chips before and after ten treatment cycles with the e-compactor.

Figure 2 shows that e-compactor treatment can significantly reduce the size of spruce chips up to fibre level, but it also separates the fibres and breaks the fibre surface into fibrils.

The results of the first tests showed that all the treatments increased the enzymatic hydrolysability of TMP (data not shown). The highest hydrolysis level in 48 hours, 30-35% of dry weight, was obtained with TMP treated chemically with NaOH, H_2O_2 or H_2O_2 with cobalt salt, and then mechanically treated 5 or 10 times using the e-compactor. For spruce, the highest enzymatic hydrolysis level was obtained with a combined NaOH and mechanical treatment. Of the pre-treated dry matter, 50% was solubilised into sugars during the enzymatic hydrolysis for 72 hours.

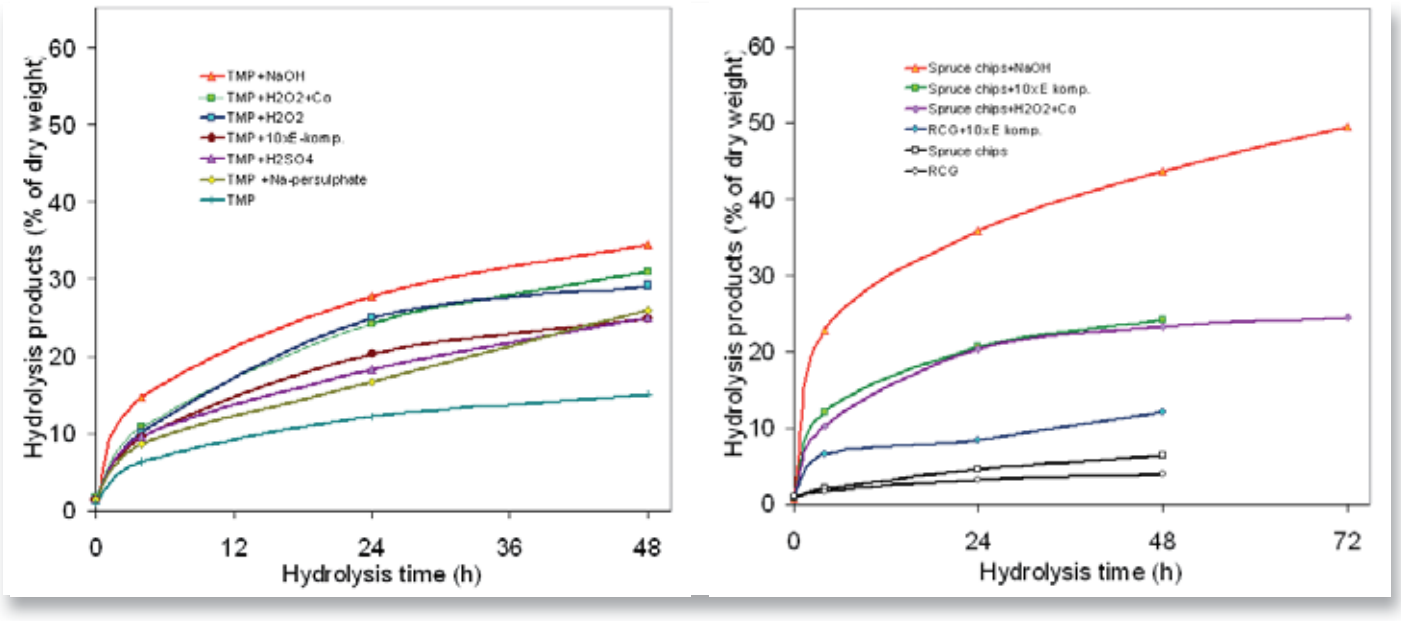

Figure 3. Enzymatic hydrolysability of pre-treated washed materials. Effect of pre-treatment of TMP (left picture) and reed canary grass (RCG) or spruce chips (right picture).

The enzymatic hydrolysability of reed canary grass without chemical treatment was very low.

The carbohydrate composition was analysed from the washed materials that gave the highest enzymatic hydrolysis levels. The polysaccharide content of the washed pre-treated materials was 50-62%. Glucose, i.e., the cellulose content of pre-treated materials, varied from 40% to 48% of the dry matter. The highest cellulose and polysaccharide content was obtained with spruce treated mechanically after peroxide-cobalt treatment. Compared with the values of untreated spruce, clear effects of pre-treatments on the carbohydrate composition could not be seen. The enzymatic hydrolysability of pre-treated raw materials in respect of the total carbohydrate content in the hydrolysis material is presented in Figure 3.

The results showed that the highest enzymatic hydrolysis level, 80% of the total carbohydrates, was obtained with spruce treated with NaOH and mechanically. With this treatment, a similar hydrolysis level and rate were obtained as that of steam explosion, which is a state-of-the-art pre-treatment technology. Compared with steam-explosion, however, this new mechano-chemical method using the e-compactor consumes less solvent and is easily scalable to production scale. In addition, the energy consumption during cellulose mass processing is quite low, varying from 70 to 20 kWh/t and decreasing after each treatment cycle. This result has led to an invention notification and patent application.

CMC Pre-treatments

These CMC treatments were conducted after discussions with the customer to find out if there was any indication that the mechano-chemical treatment using the e-compactor could be possible for their purposes and for the basis of customer projects.

The test for DP control for the CMC product led to a finding that enzymatic pre-treatment was impossible to conduct in the process due to the high water content, which can dissolve CMC before processing. The dry mechanical treatment, however, proved a promising pre-treatment method, enabling the cellulose content to increase by 8% during further processing.

Compacting trials for CMC with a high dry material content >50% and milling, according to the customer, led to a significant increase in bulk density, offering a promising new processing option.

Conclusions

This study was divided into several tasks in which the mechano-chemical dry processing method was used as pre-treatment for further processing enzymatically or chemically. The first task was to find out if combined mechano-chemical and enzymatic processing

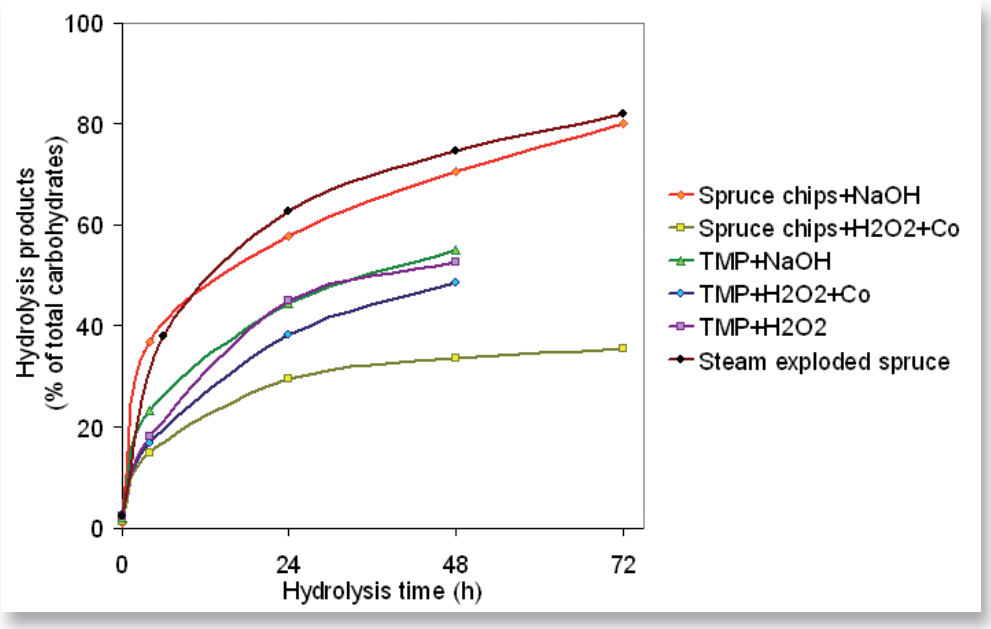

Figure 3. Enzymatic hydrolysability of mechano-chemically pre-treated spruce chips and TMP compared with steam-exploded spruce.

could lead to better alkaline solubility of cellulose carbamate made with the dry processing method. The result was that the applied enzymatic treatment caused partial degradation of the cellulose carbamate, but the alkaline solubility could not be increased to the required level, even though a small increase in alkaline solubility could be achieved. With cellulose carbamate from China, the alkaline solubility was already high without any treatments. The enzymatic treatment caused a relatively high yield loss. The enzymatic method is probably more suitable for celluloses with lower alkaline solubility or that have been modified less chemically. The biggest problem of this procedure is that carbamation is performed using dry methods (water content <50%) and enzyme treatment has to be performed with a high water content (water content >95%), so, from a processing point of view, this is not very cost-effective compared with the results obtained. In the future, when the enzymatic process may be possible with a high dry material content, this combined processing method could be used. It is also possible that different kinds of effects will be obtained with other enzymes and endoglucanase preparations.

In the second task of this preliminary study, enzymatic total hydrolysis combined with chemical and mechanical pre-treatments was evaluated. The treatment with NaOH and mechanical compacting resulted in the highest enzymatic hydrolysis rate and level. Of the total carbohydrates, 80% were hydrolysed in 72 hours. The results were comparable to those obtained with steam explosion, which is a state-of-the-art pre-treatment technology. Compared with steam explosion, however, this new mechano-chemical method using the e-compactor consumes less solvent and is easily scalable to production scale. In addition, the energy consumption during mechanical compacting was quite low, varying from 70 to 20 kWh/t and decreasing after each treatment cycle. This result leads to an invention notification and possible patent application.

The third task was to employ the mechano-chemical dry processing method for CMC pre-treatment for different modification purposes such as control of the polymerisation degree (DP) and compacting of CMC. In the DP control, enzymatic treatment was also used, but it was found not to be suitable for the total process concept due to the high water content. The dry mechanical treatment proved a promising pre-treatment method, and it enabled the cellulose content to increase by 8% during processing. Compacting trials for CMC with a high dry material content and milling led to a significant increase in bulk density and offered a promising new processing option.

This study showed the possibilities not only of dry processing methods using VTT's own compacting technology but also of combined enzymatic and dry

processing methods. As soon as the dry material content in cellulose enzymatic processing can be increased to a level >50%, these two methods together can offer new environmentally friendly processing options for several cellulose modification processes. This new compacting method can already be used as a low solvent and energy-saving process method. Besides cellulose, this method can also be applied to several other biomass processes. Calculations and process optimisation have to be made for each application separately and more precisely however.

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A novel method for improving cellulose functionality towards plasticization

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When looking at new product possibilities for cellulose fibre, one natural way is to go towards mouldable fibre-web or high-fibre-content extruded composite materials that are thermally mouldable. These materials can be processed with plastic processing methods allowing plastic-type packaging materials with high mouldability and shapes, those are completely new for high cellulose-content materials.

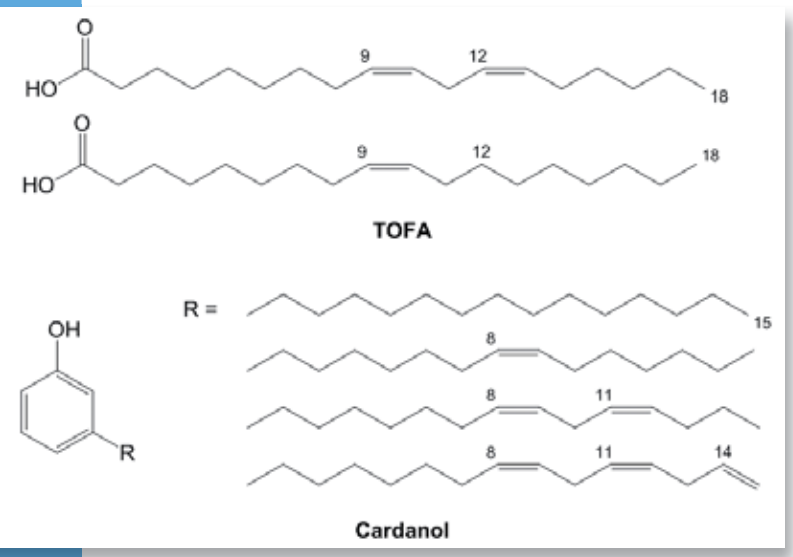
One challenge of combining highly hydrophilic cellulose and hydrophobic plastic materials is poor adhesion, which restricts film-forming properties and gives low impact strength to these materials. The use of typical plasticizers also often impairs temperature resistance, impact resistance and water absorption properties, and plasticisers have a tendency to migrate on the material surface. This can be avoided by cross-linking cellulose and plasticizer and/or coupling those to matrix polymers. Reactions to cellulose fibre are normally carried out using different solvent processing methods. These are often time-, energy- and solvent-consuming. To minimise the amount of solvent and the processing steps, we applied dry processing methods for cellulose modification and plasticization. By using the dry compacting method, we were able to add plasticizers and reactants to moist or dry cellulose fibre before processing it reactively in plastic processing equipment such as compounders with the aim of obtaining good compatibility with polylactic acid (PLA). These dry processing methods can be a way of introducing equivalent amounts of reactants to cellulose and also enabling the use of moisture-sensitive reactive additives. We introduced dispersants and reactive plasticizers/additives containing anhydride, epoxy, hydroxyl or lactone functionalities. Processing methods such as dry compacting, reactive extrusion, injection moulding, sheet extrusion and thermal mould pressing were used.

As a result of this project, mould-pressed thermoformable materials with PLA and 30% cellulose fibre content were made using epoxide- or anhydride-functional additives. Compared with earlier attempts by the WoodWisdomNet research Funfirebic1, the maximum amount of fibre was 10%. An invention notification (KI010227) was submitted relating to result presented here. Other successful result related to the impact properties of biocomposites containing PLA and 30% cellulose fibre with plasticizers. The impact strength with anhydride-functional Anhydride1 was increased by 25%, and with hydroxyl-functional Hydroxyl1 and Epoxy2(Elastomer) by about 30%. The highest increase in impact strength of 92-106% was achieved with epoxy-functional natural-oil-based plasticizers made using VTT's own technology, and this result also led to an invention notification.

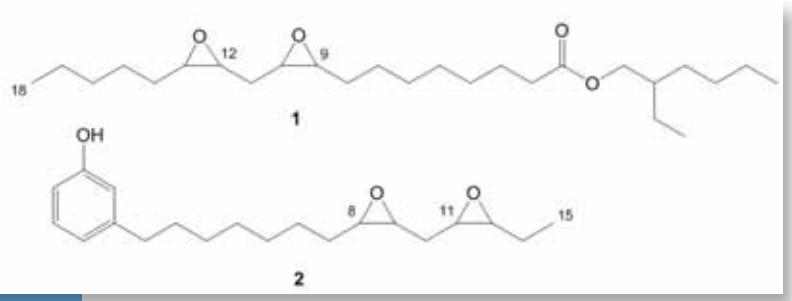
The main result of this study, however, is knowledge about suitable chemistry that can be used for coupling hydrophilic fibres and hydrophobic polymers so that the elastic and impact properties of the resulting biocomposite materials can be improved. This knowledge can be further used in joint and EU projects as well as in the development of natural-oil-based coupling agents with VTT's own technology.

Materials and methods

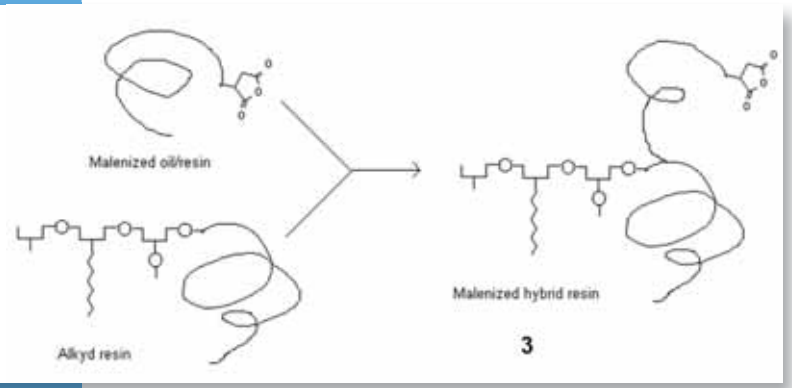
The polymeric matrix material used in this project was PLA 2002D (NatureWorks), which is polylactide-tailored for film purposes. Birch pulp (VTT/KCL) was used as the fibre material. It was torn into pieces from a sheet using a blade mill with 15 mm holes. Altogether, fifteen additives with different functionalities were tested as reactive plasticizers or cross-linkers in compounds: seven different epoxides, two anhydrides, two hydroxyl-functional, one lactone-functional and two dispersants. The additives were selected according to their ability to react or attach to the cellulose fibre surface and modify the surface properties, work as cross-linkers between cellulose and matrix polymers or improve the dispersion ability of cellulose fibres to matrix polymers. Three of the natural oil, TOFA of Cardanol-(Scheme 1) based additives were pre-



Scheme 1. Main components of TOFA (for2) and cardanol.



Scheme 2. Average structures of TOFA 2-ethyl hexanoate (1) and cardanol (2) epoxides.



Scheme 3. Anhydride-modified TOFA alkyd (3).

pared at VTT: one anhydride and two epoxide-functional additives according to reaction Schemes 2 and 3.

The functionalization of TOFA and cardanol was targeted at the various double bonds, which were transformed into epoxides and/or anhydrides (1-3, Schemes 2-3). The epoxidation was achieved with excellent to good yields (>80%). A conversion of ~100% of the double bonds into epoxy groups was obtained with TOFA, whereas a conversion of only ~75% was reached with cardanol. The anhydride functionalization of TOFA was performed using alkyd base and anhydride-modified TOFA. The mixture was reacted to obtain the polymeric product with reactive anhydride groups.

Mechano-chemical modification and processing

The whole processing procedure was conducted in as dry conditions as possible using mechano-chemical methods and plastic processing equipment. The first stage of the dry processing was based on VTT's own technology[2] using the modified pelletising equipment e-compactor, which allows low water content fibre material processing without increasing the friction temperature too much for sensitive carbohydrate materials. There is still a small temperature increase, which, combined with pressure, can lead, already at this stage, to some reactions between the additives and the cellulose. Dried fibre-additive pellets were compounded using a Berstorff ZE 25 x 33 twin-screw extruder followed by injection moulding with the Engel 200/50HL into dog-bone shaped test bars. Compounds were also extruded into 10-cm-wide sheets with a Brabender one screw extruder followed by thermal mould pressing to a 1-cm-deep, 7-cm-diameter round-shaped cup form. Tensile strength tests were conducted according to standard SFS-EN ISO 3167:2003 and Flexural strength according to ASTM D790-02 using Instron 4505 and Charpy impact strength (unnotched) according to standard ISO179. The interactions between the fibre, additive and polymer were checked using DSC (TA Instruments model MDSC2920) and dissolving out the PLA matrix.

Results and discussion

The tensile strength, impact strength, flexural strength properties and thermal behaviour (DSC) were analysed for all the processed materials. The film extrusion and mould processing properties were also tested.

Of the tensile strength results, the best tensile strength and toughness was retained with the epoxy-function-

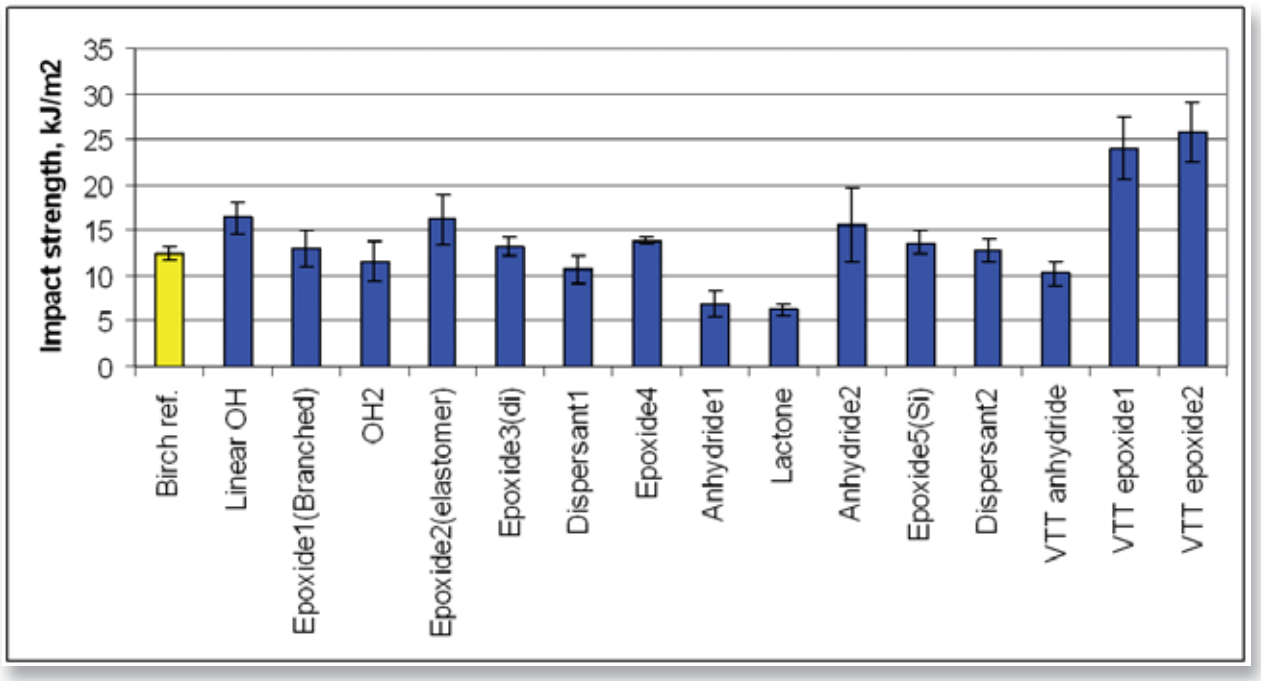


Figure 1. Impact strength results for PLA birch pulp composites with 7.5% additive and a fibre content of 30%.

al additives Epoxy5(Si)Silikopon, Epoxy1(branched), Epicote3(Di), and materials with a mainly dispersion/plasticizing ability. With Lactone functionality and Epoxide4, the module remained almost at the original level regardless of the 50% drop in tensile strength, indicating quite a rigid material. The strain results showed an increase in the strain at break with additives such as Hydroxyl1 and Hydroxyl2, all epoxides and Anhydride2. These materials, except the VTT epoxides, also exhibited a clear difference between the strain at max strength and the strain at break. This indicates that there is some cross-linking, either covalent or hydrogen bonding, between the polymer, additive and cellulose. The mainly dispersing additives did not have any effect on the strain. The additives Lactone and Anhydride1 clearly had a negative effect on the strain, which dropped more than 50% compared with the reference, without improving the tensile strength properties.

The impact strength results are presented in Figure 1.

The impact strength results presented in Figure 1 shows that the effect of additives based on VTT's own natural oil derivatives increased the impact strength by 92-106%, which is quite a significant increase. About 30% of the increase was achieved with Hydroxyl1 and Epoxide2 (Elastomer). Anhydride1 gave an increase of about 25%, and Lactone and Anhydride2 caused a 50% and 45% drop respectively. Other additives had no significant effect on the impact strength results.

The flexural strength results showed no improvement from the additives, and the results closely resembled the tensile strength results from the point of view of the additive effect. The highest results in strength and module were obtained with Epoxy5(Si), which had the same strength value (103 MPa) and only about 8% lower module value (6217 MPa) than the reference without additives. The highest drop was with Anhydride1 to a strength value of 34.4 MPa and module 3842 MPa.

According to the DSC results, reactions between polymer-additive-cellulose occurred in materials containing epoxy functionality, anhydride functionality and Hydroxyl1. The reaction degree was not the issue in this study, so it was not clarified.

The main task of this study was to find out if these additive containing materials had any mouldability to film or thermal moulding ability after sheet extrusion. Due to the fairly high fibre content, the processing was relatively difficult in some cases, and with some compounds it did not succeeded at all. The compounds that could be processed into sheets were also thermally moulded. The extrusion and moulding processes were not optimised separately for any of these materials, so these re-

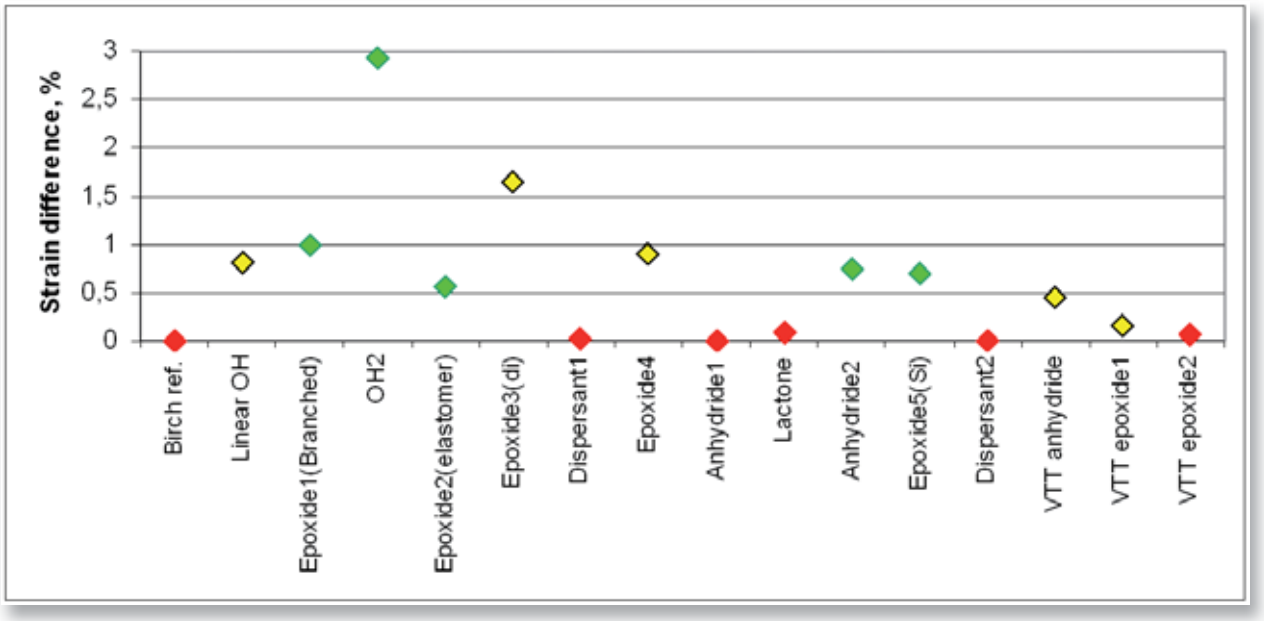


Figure 2. Correlation between the mouldability of PLA fibre (fibre content 30%) compounds and the difference in strain between max strength and strain in break during a tensile strength test. The red points ♦ are not mouldable, the yellow points ♦ are mouldable to some extent and the green points ♦ are mouldable into shapes.

sults are mainly a normative base for future work. The results of the sheet extrusion and moulding process in correlation to yield strain results are presented in Figure 2.

According to the results in Figure 2, it seems that if the cellulose-fibre-containing material has a clear yield strain, it is at least mouldable into sheet form and, in the best cases, mouldable in the thermal pressing process. This yield strain in material can be achieved through functional additives that are able to disperse fibre properly to polymers and form links between fibre and polymers through covalent or hydrogen bonds. An example of properly dispersed and easily mouldable material (PLA+30% BP+7.5% Epoxy1(branched)) can be seen in Picture 1. There was also other material (PLA+30% BP+7.5% Anhydride1) that was not as nicely dispersed though it was still mouldable.

Conclusions

The task in this project was modification and plasticization of cellulose for enhanced compatibility with biopolymers with the aim of producing materials suitable for thermally moulded applications (film extrusion, thermal mould forming and injection moulding) using combined dry compacting and reactive extrusion methods. By using the dry compacting method, we were able to add plasticizers and reactants effectively in equivalent amounts to moist/dry cellulose fibre before processing it reactively with plastic processing equipment with the aim of obtaining good compatibility with biopolymers such as PLA. This environmentally friendly dry compacting method also allows moisture-sensitive additives to be used attached with cellulose, enabling grafting or internal cross-linking between cellulose and biopolymers.

As a result, for tensile strength and flexural strength properties, it can be said that the addition of all plasticizers caused a 15-50% drop in tensile strength and a 0-66% drop in flexural strength. According to the DSC results, the reactions occurred in, at least, the epoxide, anhydride and high OH-value additive containing materials, which also explains the improved strain at break values compared with the reference material as well as the existence of elongation at yield strain in those materials. This elongation at yield strain or difference between the strain at break and the strain at max strength also seems to correlate with the sheet extrusion and mouldability properties of these composite materials.

The impact strength results of PLA + 30% cellulose-fibre-containing materials showed a clear increase with some plasticisers. The impact strength was increased by 25% with Anhydride1 and about 30% with Hydroxyl1 and Epoxy2(Elastomer). The highest impact strength increase of 92-106% was achieved with epoxy-function-

Picture 1. Thermally moulded items of PLA+30% birch pulp with 7.5% additives of Anhydride1 (top left) and Epoxide1(branched) (bottom left) and a closer look at Epoxide1(branched) (right).

al, natural-oil-based plasticisers made with VTT's own technology. This result led to an invention notification.

As the final result of this project, mould-pressed thermoformable PLA materials with 30% cellulose fibre were made using epoxide- or anhydride-functional additives of branched hydroxyl-functional additive. Epoxide1(branched) also gave quite nice dispersion of fibres in moulded material. Compared with earlier attempts without plasticizers, the maximum amount of fibre in thermoformable sheet-form material has been 10%. This is quite a significant increase in fibre content. An invention notification (KI010227) was submitted relating to this result.

The main result of this study, however, is the knowledge of suitable chemistry that can be used for the coupling of hydrophilic fibres and hydrophobic polymers so that the elastic and impact properties of the resulting biocomposite materials can be improved. This knowledge can be used further in joint and EU projects as well as in the development of natural-oil-based coupling agents based on VTT's own technology. In further projects, the applicability of additives should also be tested with more hydrophobic polyolefin-type matrices.

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Transparent paper

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Paper can be locally impregnated with biopolymers as starch esters and cellulose esters to form local translucent areas with significantly improved strength properties. Water dispersion and polymer-melt impregnation technologies can both be used for paper and board. For the first time, technology has been shown to be directly applicable to existing commercial paper grades and end products such as paper bags.

Materials and methods

The research focused on the local conversion of paper into a translucent fibre-polymer composite with the aid of a thermoplastic starch-ester filler-coating pigment-impregnation method and polymer-melt impregnation (extrusion) technology.

Dispersion impregnation

The preparation of the test sheets included: (1) preparation of wet hand sheets; (2) impregnation of both sides of the wet sheets with starch-acetate pigment spray, the intended amount of starch polymer was about 50 w-% of the original weight of the paper; (3) compression of sheets; (4) drying of sheets (23°C, 50% relative humidity) overnight and (5) treatment of dried test sheets by softener (glycerol mono-acetate) spray followed by an immediate 15 s thermal treatment at 140°C. During the thermal treatment, the pressure force caused by the cover piece was 50 N. The calendering process was also tested on its own for the treatment of starch-pigment containing hand sheets. The calendering was performed using 2 bar and 10 bar pressure at 135-140°C.

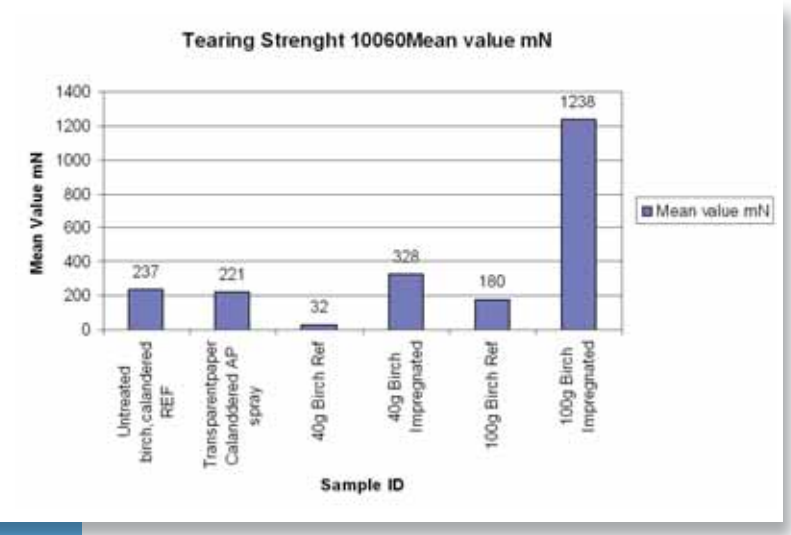

Figure.1a. Tearing strength measurement results of AP-pigment-treated sheets. The values represent more of the actual observed strength of the test material than the indexed values.

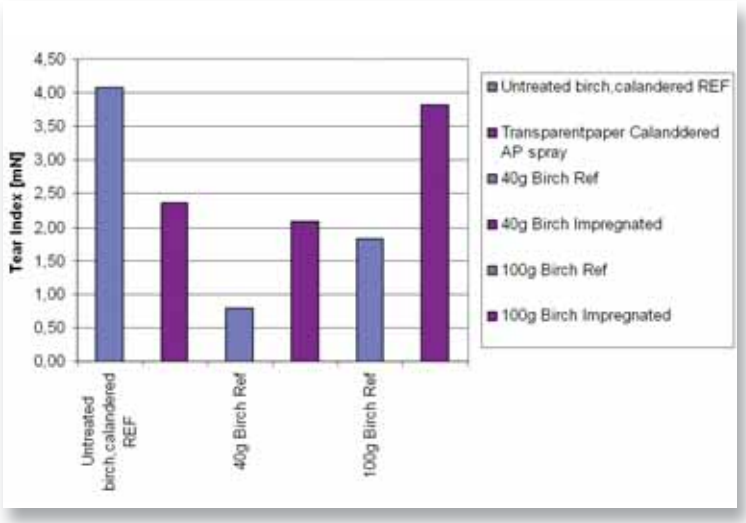

Figure 1b. Tearing strength measurement results presented as Tear Index values.

Polymer melt impregnation

Experiments were carried out using commercial cellulose acetate mixed in a ratio of 1:1 with triethyl citrate (TEC) by extruder. In addition to translucency, the mechanical strength of the end product was monitored.

Results and discussion

VTT has developed a technology for the preparation of starch-ester pigment/filler formulations and low-melt viscosity formulations of starch and cellulose esters[1,2]. The last-mentioned formulation is based on solid state oxidative cleavage of starch and cellulose esters.

At the time, technology was also applied to paper grades consisting of unbleached cellulose fibre. The overall aim was to show that the method is, by and large, applicable to commercial paper end products like paper bags or carton packages. In addition to the translucency of the paper, the mechanical strength of the treated area of paper was monitored. Tests were carried out using standard methods for the determination of the mechanical properties of the paper.

Strength of acetyl starch pigment- (AP) impregnated papers

Tearing strength results are presented in Figures 1a and 1b. The results clearly show the increased tearing strength of the material, which was an expected result indicating that the material is actually a fibre-polymer composite.

Translucency of starch-pigment-treated paper

Figures 2a and 2b illustrate the effect of starch polymer and softener on paper translucency. In this experiment, the starch polymer was oxidized starch acetate (MOX)[3], which has an original amylose content of 60%. The amount of starch polymer was 50w-%.

The results show that the compatibility of starch polymer and glycerol mono-acetate (monoacetin) is satisfactory when softener is added as a post-treatment to paper (Figure 2a). When a reference sheet (Figure 2b) was treated with softener, the migration of the softener was observed, and the initial translucency of the area treated with softener reduced. These results strongly indicate that thermoplastic polymer is superior to low molecular weight compounds, especially when considering the permanency of the translucency and strength properties of the material.

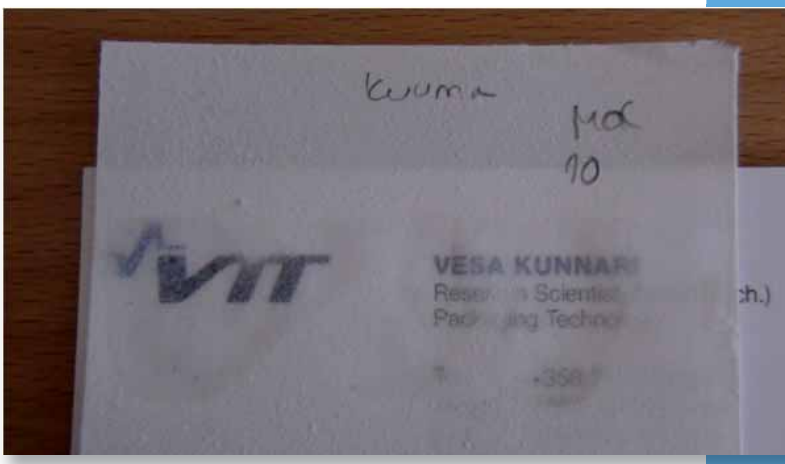

Figure 2a. MOX+ monoacetin.

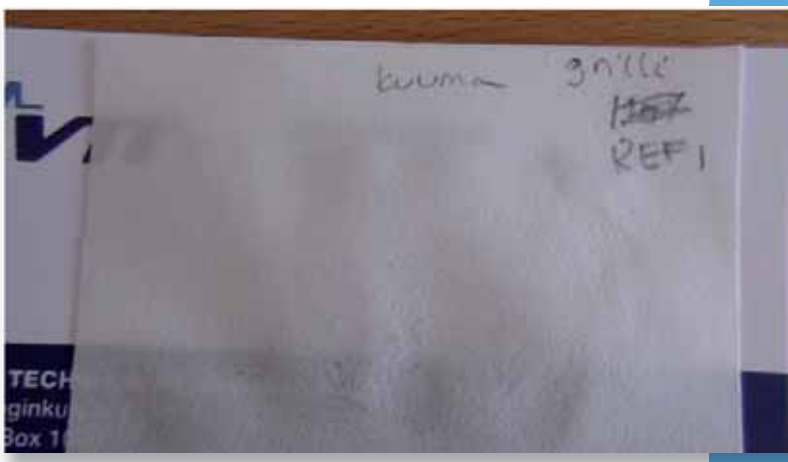

Figure 2b. Monoacetin softener on its own.

Calendering of test sheets does not result in the formation of a translucent area, which is a strong indication that the softening aid of polymers is required. Calendering resulted in the formation of a smooth surface, however, which corresponds well with earlier results of acetylated starch pigments1. The impregnation of thin paper sheets (40-60 g/m^2) with starch pigments and appropriate softeners seem to be a promising technology for producing locally translucent areas.

Melt-impregnation of paper

The method is based on the use of compounded plastic films that are thermally melted and pressed into a fibre matrix. The method is found to be suitable for paper and board up to 200 g/m^2. The results of pigment impregnation are compared with polymer-melt impregnation. The results are presented in Table 1.

Table 1. Mechanical strength of translucent paper and board prepared by melt impregnation and pigment dispersion impregnation. Symbols: CD = Cross-direction, MD = Machine direction. 'F' and 'Brown bag' are commercial paper products for bread packaging.

Sample	Mean Tensile Strength (N/m)	Tensile Index (Nm/g)	Modulus of Elasticity E (N/mm^2)
Untreated birch clendered_Ref	2370	40.7	4240
Transparent paper_calendered_AP_spray	2290	24.5	3650
40g_Birch_Imp	2370	15.1	1060
40g_Birch_Ref	611	15.1	1170
100g_Birch_Impregnated	5870	18.1	1410
100g_Birch_Ref	1440	14.6	1500
F_Imp_CD	**3260**	16.5	1370
F_Imp_MD	**4530**	22.9	2070
F_ref_CD	2220	46.3	3040
F_ref_MD	3500	73.1	5270
Brown_pag_Imp_CD	**2890**	15.0	1180
Brown_bag_Imp_MD	**6280**	32.5	2420
Brown_bag_Ref_CD	2270	50.6	3060
Brown_Bag_Ref_MD	5290	118	6560

Conclusions

The impregnation of thin paper sheets (40-60 g/m^2) with starch pigments and appropriate softeners seems to be a promising technology for producing locally translucent areas.

Polymer-melt impregnation is well suited to paper and board products up to 200 g/m^2. The technology has potential for the continuous extrusion-coating process.

The translucent area of the paper is not the weak point of the end product.

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Feasibility of atomic layer deposited Al_2O_3 barrier layers onto temperature-sensitive packaging materials

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Thin Al_2O_3 coatings were deposited at low temperatures of 80 or 100°C on various polymer-coated boards and plain polymer films using the atomic layer deposition (ALD) technique. The work demonstrated that such ALD-grown Al_2O_3 coatings significantly enhance the barrier performance against oxygen and water vapour. Even extremely thin (25 nm) barrier coatings of Al_2O_3 could be suitable barrier layers for dry food and pharmaceutical packages made from temperature-sensitive fibre-based materials. It was also demonstrated that these coatings may have relatively high seal strengths when sealed against LDPE coatings or themselves. In addition, ALD-grown Al_2O_3 coating did not significantly reduce the degradability of biopolymer-coated boards in composting conditions.

Introduction

Growing environmental concerns related to the use of synthetic polymers in the packaging industry have led to the need for new, especially bio-based, materials in such applications[1]. Currently, synthetic polymers are widely used in packaging applications because of their relatively low cost and high performance. Packaging materials from biopolymers have many advantages over their synthetic competitors, such as sustainability and recyclability[2]. In addition, fibre-based packaging materials have a high stiffness vs. weight ratio. Poor barrier properties and sensitivity to moisture are the main challenges for the extended use of bio-based materials. Employing a thin surface coating is one way to improve the barrier properties and water-sensitivity of these materials.

Based on our earlier studies[3-6], an Al_2O_3 coating layer grown using the ALD technique could provide an answer to the need for high-quality pore-free barrier films. ALD is a surface-controlled, layer-by-layer, thin-film deposition technique based on self-limiting gas-solid reactions. It is uniquely suited to producing inorganic high-performance diffusion barrier coatings on porous materials as it allows for the preparation of dense and pinhole-free films that are uniform in thickness even deep inside pores, trenches and cavities of various dimensions[7].

Here, the aim was to study the suitability of ALD-grown Al_2O_3 coatings as barrier layers for compostable packaging materials. The oxygen and water vapour barrier properties, as well as the sealability and compostability properties of the Al_2O_3 coatings deposited on polymeric materials, were investigated.

Experimental details

Preparation of ALD materials

The packaging materials investigated for the barrier, as well as the sealability and compostable properties, were mainly commercial boards (provided by Stora Enso Oyj) coated with synthetic low-density polyethylene (B(PE)) and bio-based polylactide (B(PLA)). In addition, some biopolymer films were investigated. The materials tested are presented in Table 1. Our previous thermogravimetric study, performed for most of the present substrate materials[3], revealed that the polymeric materials are suitable substrates for the ALD process because they do not degrade thermally at the temperatures employed in our low-temperature ALD process for the Al_2O_3 coatings, i.e., below ~150°C.

The glass transition temperatures (T_g) of LDPE (T_g below 0°C) and PLA (T_g approx. 60°C) are below 80°C, so, under the ALD deposition conditions, both polymers are disordered amorphous or semicrystalline solids in which portions of molecules can wiggle around. The surface topographies of the substrate materials coated with LDPE and PLA varied greatly[4]. The PLA-coated boards were smoother than those coated with LDPE, apparently due to the higher polymer-coating weight of the PLA-coated boards (27-35 g/m^2) and the different fabrication process compared with the boards coated with LDPE (15 g/m^2). In our previous study, it became clear that due to

Table 1. Packaging materials used as substrates in the Al_2O_3 depositions.

Code	Description
B(PE)	Commercial polyethylene-coated board; LDPE 15 g/m^2, board 210 g/m^2
B1(PLA)	Commercial polylactide-coated board; PLA 35 g/m^2, board 310 g/m^2
B3(PLA)	Commercial polylactide-coated board; PLA 27 g/m^2, board 210 g/m^2
PLA1	Commercial PLA film, 25 µm
PLA2	Commercial PLA film, 75 µm
NFC	Nanofibrilled cellulose film; NFC; app. 60 g/m2
B(GGM)	Galactoglucomannan-coated board; GGM app. 9 g/m^2, board 200 g/m2 pigment-coated
PHB	Polyhydroxy butyrate film, 180 µm
Pectin	Pectin film made by solution casting; 160 µm

Table 2. Pristine and thin-film coated materials used in composting tests.

Code	Description
B	Board 210 g/m^2
B2 (PLA)	Commercial polylactide-coated board; PLA 35 g/m^2, board 210 g/m^2
B2 (PLA)-ALD	Polylactide-coated board with Al_2O_3 coating deposited on the PLA coated side
ALD-B2(PLA)	Polylactide-coated board with Al_2O_3 coating deposited on the non-PLA coated side
PLA2	Commercial polylactide film, 75 µm
PLA2-ALD	Commercial polylactide film with Al_2O_3 coating
PLA2-MA	Commercial polylactide film with metallic aluminium

their different surface roughnesses, the substrates accommodate different amounts of Al_2O_3 during the ALD-Al_2O_3 deposition[4].

Thin (25-50 nm) Al_2O_3 coatings were deposited at low temperatures of 80 or 100°C on various polymer-coated boards and plain polymer films. The depositions were carried out in a Picosun SUNALE™ ALD reactor. Trimethylaluminum (TMA, electronic grade purity, SAFC Hitech) and H_2O were used as precursors. High purity nitrogen (99.9999% N_2) was used as a carrier and purge gas. The deposition sequence was 0.1 s TMA pulse, 6 s N_2 purge, 0.1 s water pulse and 6 s N_2 purge. The operating pressure was 1-2 kPa. The resultant film growth rates were determined to be app. 0.1 nm/cycle on a silicon wafer Si(100). It should be emphasized, however, that because of the different polarities and functional groups of the surfaces of different polymers, the actual growth rates may deviate slightly from that determined for the Al_2O_3 coating on a flat silicon wafer[8-9]. Although the aim was to deposit only on the polymer-coated side, film growth on the uncoated side as well could not be prevented completely. The substrates were app. 10 x 10 cm^2 in size.

Characterizations

The oxygen and water vapour barrier properties were determined for all the samples by measuring the oxygen and water vapour transmission rates. The oxygen transmission rate (OTR) was measured from two to three parallel samples using humid gases at 23°C in 50% relative humidity with a Systech M8001 or Mocon Oxtran 2/20 and expressed as cm^3/m^2/10^{5}Pa/day. The water vapour transmission rate (WVTR) was measured for three to five parallel samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and expressed as g/m^2/day. The test conditions were 23°C and 75% relative humidity.

For the sealability tests, Al_2O_3 coatings with thicknesses of 30-50 nm were deposited at 80°C on B(PE). The sealability of the coatings was determined using the sealing strength tester (Labormaster HTC 3000, Willi Kopp, Germany). The sealing strengths were measured after sealing at temperatures of 110, 120, 130 or 140°C with a sealing force of 8 bars, a sealing time of 2 s, delay time of 10 s (cold-tack) and withdrawal speed of 12 m/min. LDPE-coated board without the Al_2O_3 layer was

used as a reference surface. ALD-grown Al_2O_3 surface layers and B(PE) were sealed against themselves and each other.

The compostability of ALD-grown Al_2O_3-coated boards and polymer films compared with commercial biopolymer films coated with metallic aluminium (Table 2) was studied by evaluating the disintegration in composting conditions using a modified pilot-scale test EN 14045. The composter bin (vol. 180 l) was filled with biowaste (fresh fruit and vegetable waste) and bulking agent (Figure 1). The temperature and carbon dioxide evolution were measured during composting, and aeration was adjusted to maintain optimal composting conditions. The compost was turned regularly and the degree of degradation of the samples was evaluated visually. The pH and moisture were also evaluated during composting.

As an exception to the EN 14045, square sheets of test material (2.5 x 3.5 cm) with four replicates were attached to the steel frames, which were buried in the biowaste/bark mixture as described by Vikman et al. (1995)[10]. Cellulose-based film is used as a positive control and polyethylene as a negative control (non-compostable). During 12 weeks of composting, the degradation of samples was evaluated visually and by measuring the weight loss of the samples at the end of the test.

Figure 1. Composter bin and steel frames used during the pilot-scale test.

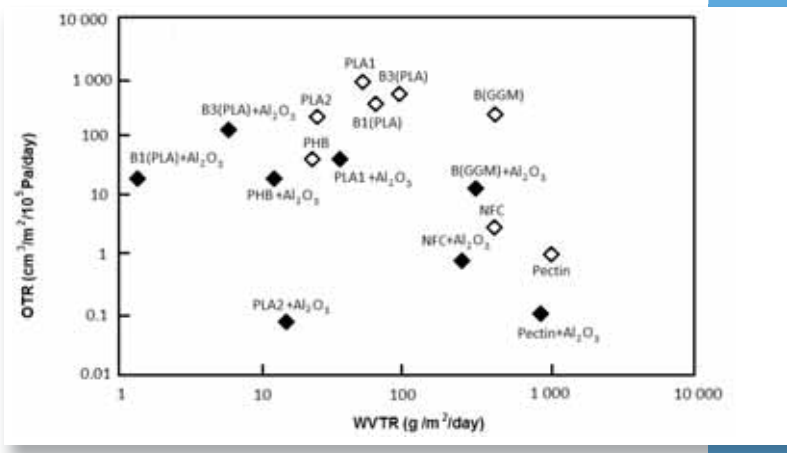


Figure 2. The most improved barrier properties of bio-based substrates achieved by the ALD-grown Al_2O_3 process.

Results and Discussion

Significantly improved barrier properties of bio-based packaging materials by thin ALD-grown layers

The oxygen and water vapour barrier properties were tested from all of the samples. The main emphasis was on the bio-based substrates. The most improved barrier results achieved so far by the ALD-grown Al_2O_3 coating are presented in Figure 2. The depositions were made at temperatures of 80 or 100°C depending on the temperature tolerance of the substrate.

Our aim was to expand the use of the ALD-grown Al_2O_3 coatings onto several of the biopolymers. The oxygen and water vapour barrier results achieved for bio-based substrates with a 25-nm-thick Al_2O_3 layer deposited by the TMA-H_2O process are summarized in Figure 2. It became apparent that Al_2O_3-coated PLA2, pectin, NFC, B1(PLA) and B(GGM) substrates are highly promising oxygen barriers and already close to the commercial oxygen barrier level for dry food applications. Besides good oxygen barrier properties, B1(PLA) with an Al_2O_3-coating was also a highly promising water vapour barrier.

In addition to good oxygen barrier properties, it was noted that nanofibrillated cellulose (NFC) film coated with a 25-nm-thick Al_2O_3 layer formed a highly homogenous layer on top of single fibres. This is believed to form protecting layers for nanofibres (Figure 3). Such materials are of high interest because of the controlled organic fibre and inorganic thin-film material integration. This kind of conformal coating on single fibres opens up new application possibilities in the area of filter development[11].

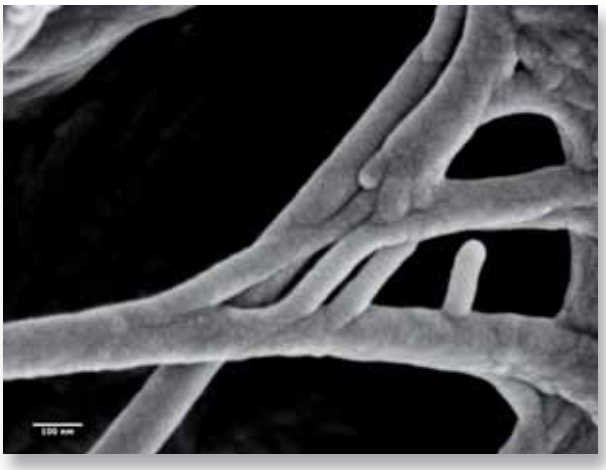


Figure 3. SEM image of NFC film coated with a 25-nm-thick Al_2O_3 layer. Nano-fibrillated fibres are uniformly coated with an Al_2O_3 layer. The smallest observed fibre thickness is app. 50 nm and the curve radius from the fibre ends is app. 25 nm.

Sealability properties of thin ALD-grown layers

LDPE-coated board B(PE) sealed perfectly against itself at all sealing temperatures. ALD-Al_2O_3 coatings slightly decreased the seal strengths when sealed against the LDPE surface. The ALD-grown Al_2O_3 coating also sealed against itself relatively well at 120-140°C. At a temperature of 110°C, LDPE was not fluid enough to displace the Al_2O_3 cover whereas at higher temperatures, the molten LDPE seemed to penetrate through the Al_2O_3 layer resulting in a sealable surface. The maximum seal strength >500 N/m was obtained with B(PE) sealed at 130°C. The 30 nm and 50 nm Al_2O_3 layers had almost comparable strengths >400 N/m when sealed against B(PE) at 120 and 130°C. The 50 nm Al_2O_3 layer prevented the penetration of molten LDPE more than the 30 nm layer, thus the seal strengths typically decreased as a function of the Al_2O_3 layer thickness.

Compostability properties of thin ALD-grown Al_2O_3 and metallic aluminium layers

The Al_2O_3 coating did not have a significant effect on the degradability of biopolymer-coated boards (B2(PLA)-ALD; ALD-B2(PLA)) (Figure 5) in composting conditions. Commercial PLA film (PLA2) degraded completely in 12 weeks, but Al_2O_3-coated PLA-film (PLA2-ALD) only degraded partly. Three of the four replicates degraded almost completely, though one of the replicates did not degraded at all. According to the criteria of EN 14045, the temperature inside the bin was high enough, though there may have been local variations in temperature. As temperature has been demonstrated to be the major factor regulating the biodegradation behaviour of polylactide[12], it could be a reason for the poor degradability of one of the replicates. Metallic aluminium -coated PLA degraded almost completely in 12 weeks.

Conclusions

Al_2O_3 films with thicknesses ranging from 25 nm to 50 nm were grown using the ALD technique at low temperature on various polymer films and polymer-coated boards. The work demonstrated that extremely thin (25 nm) Al_2O_3 coatings could be suitable barrier materials for dry food and pharmaceutical packages made from temperature-sensitive fibre-based materials. ALD-grown Al_2O_3 coatings decreased the seal strengths of LDPE-coated board. Al_2O_3 coatings did not prevent the LDPE-coated board from sealing relatively well under various sealing temperature conditions however. In addition, the Al_2O_3 coating did not significantly reduce the degradability of PLA-coated boards in composting conditions. In the future, these materials could be produced by a continu-

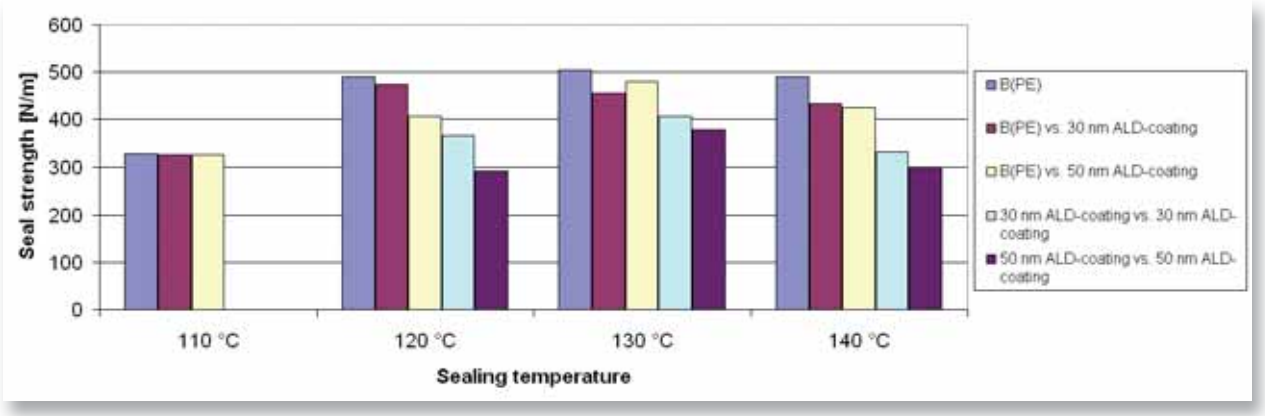
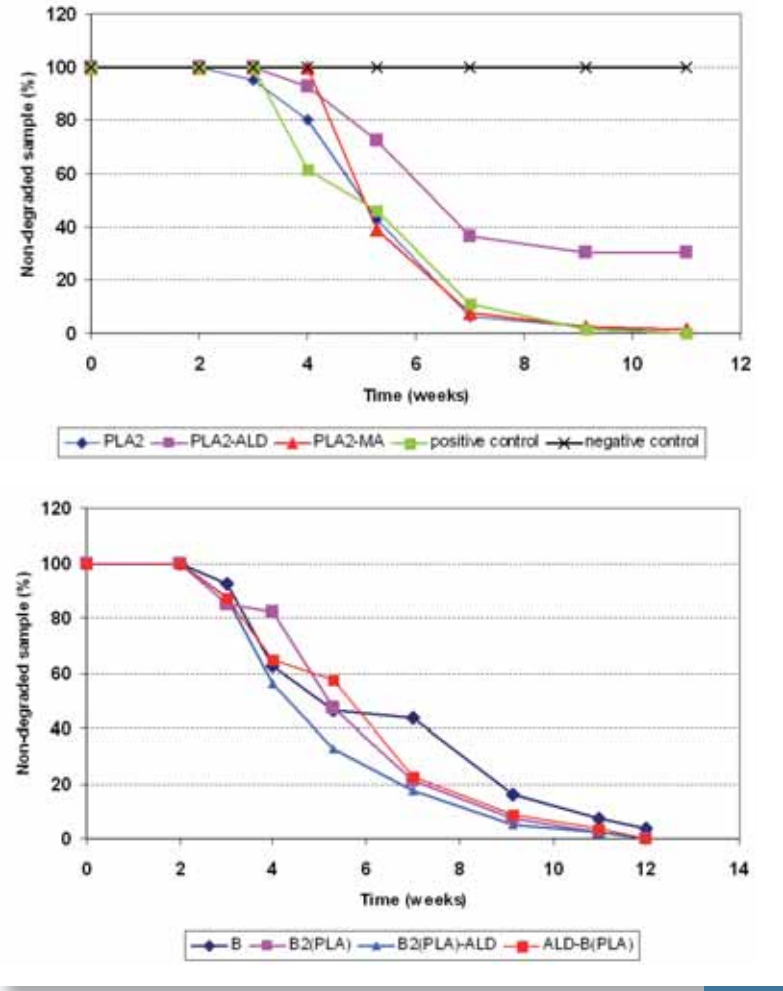


Figure 4. Sealability of ALD-grown Al_2O_3 coatings.

Figure 5. Disintegration of the samples after 12 weeks of composting (calculated on the basis of the sample area). The cellulose-based positive control degraded completely and the negative control polyethylene did not show any signs of degradation in 12 weeks, indicating that the test was successful.



ous ALD process. There are already research tools and patents available concerning the development of the continuous ALD process[13-15].

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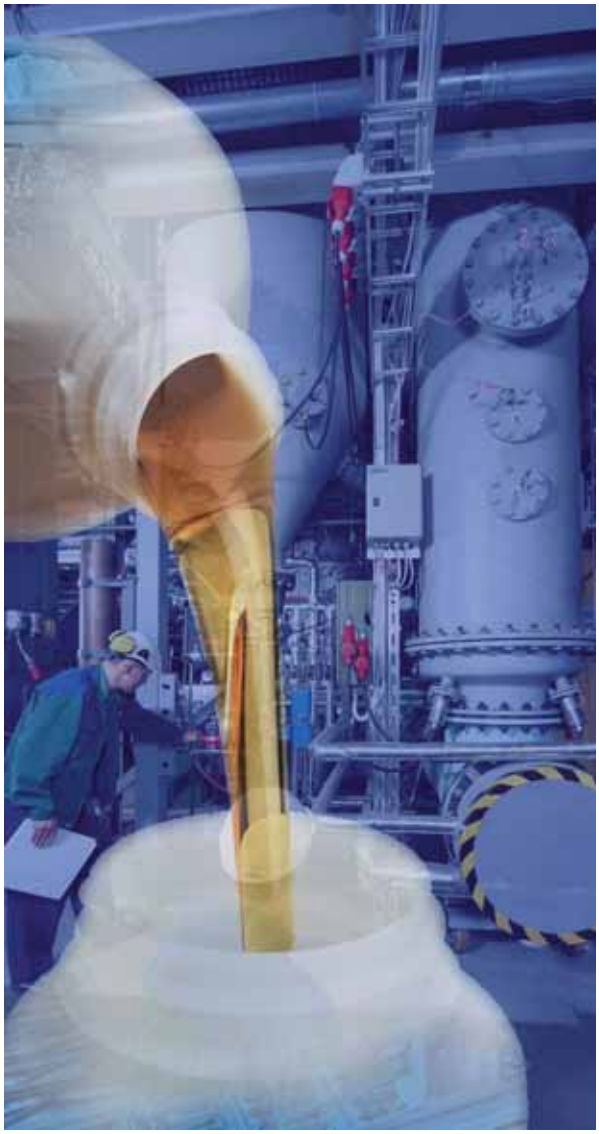
Industrial biomaterials

Industrial application of materials produced using renewable raw materials generates new, sustainable value chains and reduces our dependency on oil and the carbon footprint of consumption.

VTT's Industrial Biomaterials spearhead programme develops technologies and competencies utilising skills in chemistry, process technology, material science, modelling and analytics. The technologies and competencies developed in the spearhead programme are steered towards generating value chains that start from forest biomass and end up in selected high-volume consumer products. In such development, the key not to disturb the fragile value chains of the food sector.

The spearhead programme focuses on the development of materials and production technologies based on fibres and nanocellulose, as well as biomass-based monomers and polymers. The aim is to integrate these new value chains into existing biorefineries.

The results will be exploited by actors in the chemical, process technology and material sectors, both domestic and global. Especially interesting target sectors are the plastics, process, forest and energy industries, as well as packaging and building. The spearhead programme will cooperate closely with the Finnish strategic centres for science, technology and innovation, namely Forestcluster Ltd., Cleen Ltd. and Fimecc Ltd.



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VTT Technical Research Centre of Finland is the largest multitechnological applied research organization in Northern Europe. VTT provides high-end technology solutions and innovation services. From its wide knowledge base, VTT can combine different technologies, create new innovations and a substantial range of world class technologies and applied research services thus improving its clients' competitiveness and competence. Through its international scientific and technology network, VTT can produce information, upgrade technology knowledge, create business intelligence and value added to its stakeholders. VTT is a non-profit-making research organization.

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Kalevaprint Oy, 2011